Effect of Process Parameters on Conversion and Selectivity for the Synthesis of Dibenzyl Sulfide Using Hydrogen Sulfide and Solid Reusable Tri-Phase Transfer Catalyst

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by

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राष्ट्रीय प्रौद्योगिकी संस्थान राउरकेला

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CERTIFICATE

This is to certify that the thesis entitled **"Effect of Process Parameters on Conversion and Selectivity for the Synthesis of Dibenzyl Sulfide Using Hydrogen Sulfide and Solid Reusable Tri-Phase Transfer Catalyst",** submitted by Thadela Srinivas to National Institute of Technology Rourkela, in fulfillment of the requirements of the degree of Master of Technology in Chemical Engineering is a bonafide record of the research work carried out by him, in the Department of Chemical Engineering, National Institute of Technology, Rourkela under my supervision and guidance. Mr. Srinivas has worked on this topic from July, 2012 until April, 2013 and the thesis, in my opinion, is worthy of consideration for the award of the degree of "Master of Technology" in accordance with the regulations of this Institute. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

Date: 24th May, 2013

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Thadela Srinivas

DECLARATION

I certify that

a. the work contained in this thesis is original and has been done by me under the guidance of my supervisor.

b. the work has not been submitted to any other Institute for any degree or diploma.

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List of Abbreviations

BC	Benzyl Chloride
BM	Benzyl Mercaptan
DBS	Dibenzyl Sulfide
DEA	Diethanolamine
DIPA	Diisopropanoloamine
GLC	Gas Liquid Chromatography
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
OVAT	One variable at a time
ppm	Parts per million
ppmv	Parts per million by volume
PTC	Phase Transfer Catalysis
TEA	Triethanolamine
TPC	Tri Phase Catalyst

Abstract

Hydrogen sulfide (H_2S) is often found in the by-product gas-streams of many petroleum and natural gas processing industries. Conventionally it is being used for the production of elemental sulfur by Claus Process which is further utilized in the production of sulfuric acid or rubber industries. But Claus process is an energy-expensive process as it requires a high amount of energy and process control over oxygen and H_2S ratio. H_2S-laden gas can be utilized well by absorbing into aqueous alkanolamine and then use this reagent as a sulfiding agent to produce organo-sulfur compounds like thioether, mercaptans, disulfides etc., which have higher usability and better market value. These organo-sulfide such as Dibenzyl sulfide (DBS) find their application in pesticide, polymer, pharma and drug industries. Since the alkanolamine and benzyl chloride are two different phases and to carry out this triphasic reaction, phase-transfer-catalyst (PTC) has been used and often the application of PTC gives enhancement in reaction rate, more conversion for reactants and better selectivity of desired products.

This work was undertaken to study the synthesis of Dibenzyl Sulphide (DBS) and Benzyl Mercaptan (BM) using H_2S-rich monoethanolamine (MEA) and benzyl chloride (BC) under Liquid-Liquid-Solid phase transfer catalysis with a tri-phase catalyst.Owing to its solid state, availability, cost and reusability, Amberlite IR 400 is selected as a PTC. A parametric study was carried out which emphasized upon the impact of catalyst loading as one of the process variables on the conversion of benzyl chloride and selectivity of DBS and parametric study with these substances revealed more that 90% selectivity for desired product at ambient condition. The effects are utilized to establish a suitable mechanism of the reaction to explain the course of the reaction.

The overall objective of this study is to maximize conversion of reactant BC, maximize selectivity of desired product DBS. Reaction time, temperature, catalyst loading, stirring speed, reactants concentration and solvent concentration were chosen as parameters. These techniques can be used as an alternative to Claus process and also can act as a green route for synthesizing value-added fine chemicals like DBS, Benzyl mercaptan (BM) etc.

Keywords: Hydrogen Sulfide; Alkanolamines; Dibenzyl sulfide; Benzyl mercaptan; Liquid-Liquid-Solid Phase Transfer Catalysis; Mechanism; Selectivity; Conversion.

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INTRODUCTION

Chapter 1

Introduction

Abstract

This chapter involves a broad overview of the present research work and its vitality. It includes introduction to the sources of hydrogen sulfide, need to polish it off and retrieval.It also envisages upon the conventional process used in the industries, the objectives of this study and a note on the structure and organization of the thesis.

1.1. Anthropogenic Routes to Hydrogen Sulfide

About 10-12% of the total global discharges of the Hydrogen Sulfide (H_2S) were attributed by human deeds. H_2S is found both naturally and from human-made industrial processes. It is in the form of gases from volcanoes, sulfur springs, undersea vent, salt marshes, swamps, and stagnant bodies of water and in the crude petroleum and natural gas. The gas occurs naturally in coal pits, sulfur springs, gas wells, and as a product of decaying sulfur-containing organic matter, particularly under low oxygen conditions. And is also commonly come across in places such as municipal sewers, sewage treatment plants (H_2S is often called sewer gas), swine containment, manure stockpiles, manure-handling operations, mines, hot springs, and the holds of fishing ships.

H_2S may account for up to 1 % by volume of landfill gas emissions, although typically the percentage is much less. The formation of hydrogen sulfide within a landfill depends on certain conditions including moisture content, temperature, and pH; anaerobic conditions (lacking oxygen); and a sulfate source.

Industrial sources of H_2S comprise petroleum refineries, natural gas extraction plants, petrochemical plants, coke oven plants, chemical manufacturing and waste disposal, pulp and paper manufacturing (Kraft paper mills using the sulfate method), food processing plants, rayon textile production, wastewater treatment plants and leather tanneries.

During the course of abundant processes in the petroleum, coal, and natural gas processing industries, one or more gaseous by-products containing hydrogen sulfide H_2S are rather commonly produced. In industries, Hydrodesulfurization stands widely established

process used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. By far the largest industrial pavements to H_2S occur in petroleum refineries. The supply of light and easy-to-process crude oils are slowly deteriorating and the refiners throughout the world are forced to process heavy crude containing high amount of sulfur and nitrogen. With strict environmental guidelines and concerns, refiners are also forced to hydrotreat such crude to bring down the sulfur and nitrogen concentrations to the agreed levels. During hydrotreatment of heavy and sour crude, large amounts of H_2S is formed. In addition, during the sequence of several processes in the coal processing industries, one or more gaseous by-products containing H_2S is quite normally produced. The coal gas contains near about 0.3-3% H_2S as the main non-hydrocarbon impurities. Moreover, in the natural gas industry, the H_2S content of certain gas streams recovered from natural gas deposits in many areas of the world is often too high for viable acceptance. The composition of raw natural gas diverges widely from field to field. The H_2S content may vary from 0.1 ppm to 150,000 ppm. Other anthropogenic sources of hydrogen sulfide include coke ovens, paper mills (Kraft technique – using the sulfate method), and tanneries.

Bacteria found in our mouth and gastrointestinal tract produce H_2S during the digestion of food containing vegetable or animal proteins.

1.2. Requirement for Treating of H_2S-laden Gas

With an increase in the global environmental awareness, chemical industries are facing severe complications with the dumping of environmentally hazardous materials like H_2Sin atolerable manner.The removal of H_2S from gas and fluid streams is anticipated for a variety of reasons, such as:

- Hydrogen sulfide is a highly toxic and combustible gas with explosion limits ranging from 4.3 - 46 %. Being heavier than air, it tends to agglomerate at the bottom of ill ventilated places. Although very pungent at first, it quickly reduces the sense of smell, so potential victims may be unconscious of its existence until it is too late. For safe management procedures, a hydrogen sulfide material safety data sheet (MSDS) should be consulted. Different standards of H_2S emissions and its warning signs were shown in Table 1.1. and Table 1.2. respectively

Table 1.1. Standards of H_2S emissions

Occupational Exposure Limit (8 h time weighted average)	10 ppm
Public Exposure Limit (for the general population)	0.03-0.006 ppm
Maximum Emissions Limit from Sulfur Recovery Units	
• 1500 ppmv of sulfur compounds calculated as SO_2	
• 10 ppmv of H_2S.	
• 200 pounds per hour of sulfur compounds calculated as SO_2	

Table 1.2: H_2S Warning Signs

Concentration in parts per million (ppm)	Observations and health effects
Less than 1	Most people smell "rotten eggs."
3-5	Odor is strong.
20-150	Nose and throat feel dry and irritated. Eyes sting, itch, or water; and "gas eye" symptoms may occur
150-200	Sense of smell is blocked (olfactory fatigue).
200-250	Major irritation of the nose, throat, and lungs occurs, along with headache, nausea, vomiting, and dizziness. Prolonged exposure can cause fluid buildup in the lungs (pulmonary edema), which can be fatal.
300-500	Symptoms are the same as above, but more severe. Death can occur within 1 to 4 hours of exposure. Above 500 Immediate loss of consciousness. Death is likely to be immediate

The removal of H_2S from fluid streams can be desirable for a variety of reasons, such as:

- H_2S is odiferous in nature, corrosive in the presence of water and poisonous in very small concentrations. Therefore, it must almost completely be removed from the gas streams before use and preferably before transport. As a result, many pipeline specifications limit the amount of H_2S to less than 0.25 g/100 ft^3 of gas (Thomas, 1990).
- The presence of H_2S in the refinery gas streams can cause a number of detrimental problems in subsequent processing steps such as corrosion of process equipment, deterioration and deactivation of the catalysts, undesired side reactions, increase in the process pressure requirements, increase in the gas compressor capacity, etc. (Hamblin, 1973).

Table 1.3 Exposure Limits of H_2S (US Department of Labor)

Occupational Health and Safety Administration (OSHA) Permissible Exposure limit (PEL) for general industry	10 ppm
American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV)	10 ppm
National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)	10 ppm
NIOSH Immediately Dangerous To Life or Health Concentration (IDLH)	100ppm

1.3. Industrial Processes for the Removal and Reclamation of H_2S

Industries have to decrease the H_2S fillings of the byproduct gas streams beneath the safe limit in order to safeguard environmental safety and health safety for their worker. In industries, multiple processes have been established for the elimination and retrieval of H_2S from gas streams. Since H_2S is acidic (weak acid) in nature, its removal can be done by using an alkaline solution. A strong alkaline solution like sodium hydroxide, however, forms irreversible chemical reaction products with H_2S and thus can't be employed for the removal of H_2S from gas streams particularly if the gas contains both H_2S and CO_2 where the

concentration of CO_2 is more than 4% (Robin, 1999). This leads to the use of a weak alkaline solution like ammonia and alkanolamines for the removal and retrieval of H_2S.

1.3.1. Ammonia-based Processes

Usage of aqueous ammonia in the elimination of H_2S from gas streams had been well practiced (Hamblin, 1973 and Harvey and Makrides, 1980).Gas streams comprising both H_2S and NH_3 pass through a H_2S scrubber and an NH_3 scrubber in sequence as shown in Fig.1.2. Stripped water is fed to the top of the NH_3 scrubber where it absorbs NH_3 from the gas. The resulting NH_3 solution is then used as absorbent for H_2S in the H_2S scrubber. The rich solution, from this unit comprising ammonium sulfide in solution, is fed to a deacidifier, which decomposes the ammonium sulfide to yield the H_2S rich vapor and NH_3 rich liquor.

The usage of ammonia to remove H_2S and CO_2 from gas streams has deprived of in recent years; however, the process is still used to desulfurize coke-oven gas in a number of installations. The NH_3-based H_2S removal processes are offered by the Krupp Wilputte Corporation (1988), Davy-still Otto (1992), and Mitsubishi Kakoki Kaisha Ltd. (1986) (Kohl and Nielsen, 1997). Although, these processes vary in the particulars of heat exchange, recycle streams, wash steps, hardware design, and process conditions, the chemical reactions and the basic operation are basically the same as specified earlier. The reactions happening in the system comprised of ammonia, hydrogen sulfide, and water can be represented by the following equations (Scheme 1.1).

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$NH_3 + H_2S \rightleftharpoons NH_4HS$$

$$2NH_3 + H_2S \rightleftharpoons (NH_4)_2S$$

Scheme 1.1

Some of the notable advantages with the NH_3-based process over amine-based process (Kohl and Nielsen, 1997):

- The NH_3-based process is appropriate for gas streams comprising both H_2S and NH_3, as simultaneous removal of NH_3 is obvious in this process. Besides, for the gas streams containing both H_2S and NH_3, the removal of both impurities might be

completed in a solitary step in the ammonia-based process instead of two steps as in the situation of alkanolamine-based process.

- The rate of absorption of H_2S into aqueous NH_3 solution is fast and reliant upon the concentration of NH_3. Therefore, with acceptable NH_3 concentration at the interface, it is possible that the gas film resistance governs the rate of absorption of H_2S. On the other hand, absorption of CO_2 in weak alkaline solution like aqueous NH_3 is considered typical of a liquid film controlled system. The consequence is that when gases containing both H_2S and CO_2 are contacted with aqueous NH_3 solution, the H_2S is absorbed much more rapidly than the CO_2. Yet another aspect is that once in solution, the CO_2 is stronger acid than H_2S and under equilibrium conditions, process would essentially be expected to be selective for CO_2. Therefore, by using aqueous NH_3, the selective absorption of H_2S or CO_2 is possible from the gases containing both H_2S and CO_2. By the practice of spray column in combination with short contact time can lead to the selective absorption of H_2S from the gas mixture containing both CO_2 and H_2S.

- NH_3 has the advantage for such applications being essentially unaffected by the presence of carbonyl sulfide (COS), carbon disulfide (CS_2) and hydrogen cyanide (HCN).

Regardless of these advantages, the use of ammonical scrubbing has not been globally accepted in the gas treating art as the preferred method for removing H_2S from a gas stream. This is primarily because of a number of operational problems associated with its implementation (Hamblin, 1973), such as:

- High partial pressure of NH_3 forces the scrubbing step be conducted with relatively dilute NH_3 solutions or at relatively high pressures or a separate water wash step after the NH_3 scrubbing step in order to remove NH_3 from the treated gas stream. In addition, the use of dilute scrubbing solutions typically increases substantially the regeneration costs where the regeneration step is conducted at a considerably higher temperature than the scrubbing step.

- Another trouble is associated with the renewal of the rich absorbent solution withdrawn from the scrubbing step. Several regeneration procedures have been projected but they typically have involved the use of soluble catalysts such as

hydroquinone and have had difficulties such as contamination of the sulfur product with the catalyst, excessive formation of side products such as ammonium sulfate and thiosulfate and loss of scrubbing solution and catalyst during the periodic purges that are generally required to remove side products from the system. Other difficulties have been associated with the recovery of the elemental sulfur from the regeneration step where it has been usual to form a froth of sulfur, which then must be skimmed off and filtered.

1.3.2 Alkanolamine-based Process

Although both ammonia- and alkanolamine-based processes are in usage for the elimination of acid gas constituents (H_2S and CO_2) from gas streams, alkanolamine-based process got wide commercial acceptance as the gas treating art because of its advantages of low vapor pressure (high boiling point) and ease of reclamation. The low vapor pressures of alkanolamines lead the operation extra flexible in terms of operating pressure, temperature, and concentration of alkanolamine in addition to the insignificant vaporization losses.

Triethanolamine (TEA), which wasthe first alkanolamine to become commercially available, was used in the early gas-treating plants (R. R. Bottoms, 1930). The amines that have proved to be of principal commercial interest for gas purification are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Triethanolamine has been displaced largely because of its low capacity (resulting from higher equivalent weight), its low reactivity (as a tertiary amine), and its relatively poor stability. However, frequently used alkanolamines, such as MEA and DEA, are not selective to H_2S in their reaction. The alkanolamines absorb the total acid gas components present in the gas streams, e.g., CO_2, as well as H_2S. Such non-selectivity is not required in the present application.

Diisopropanolamine (DIPA) (Bally, 1961; Klein, 1970) is being used to some extent in the Adip process and in the Sulfinol process as well as in the SCOT process for Claus plant tail gas purification. However, methyldiethanolamine (MDEA) is slowly displacing DIPA in these applications. Although MDEA was described by Kohland coworkers at Fluor Daniel (Frazier and Kohl, 1950; Kohl, 1951; Miller and Kohl, 1953) as a selective absorbent for H_2Sin the presence of CO_2 as early as 1950, its use in industrial processes has only become important in recent years. A somewhat different type of alkanolamine, 2-(2-aminoethoxy) ethanol, commercially known as Diglycolamine (DGA), was first proposed by Blohm and Riesenfeld (1955). This compound couples the stability and reactivity of monoethanolamine

with the low vapor pressure and hypscopicity of diethylene glycol and, therefore, can be used in more concentrated solutions than monoethanolamine.

In addition to simple aqueous solutions of the previously mentioned alkanolamines, proprietary formulations comprising mixtures of the amines with various additives are widely used. Formulated solvents are offered by Dow Chemical Company (GAS/SPEC), UOP (and or Union Carbide Corp.) (Amine Guard and UCARSOL), Huntsman Corporation (formerly Texaco Chemical Company) (TEXTREAT), and BASF Aktiengesellschaft (Activated MDEA). Some of Dow's GAYSPEC and UOP's Amine Guard formulations are basically corrosion inhibited MEA and DEA solutions. However: the most significant development in formulated solvents is the advent of tailored amine mixtures. These are usually based on MDEA, but contain other amines as well as corrosion inhibitors, foam depressants, buffers, and promoters blended for specific applications. They can be designed to provide selective H_2S removal, partial or complete CO_2 removal, high acid gas loading, COS removal and other special feature (Manning and Thompson, 1991; Pearce and Wolcott, 1986; Thomas, 1988: Meissner and Wagner. 1983; Meissner, 1983; Niswander et al., 1992).

A different class of acid gas absorbents, the sterically hindered amines, has recently been disclosed by EXXON Research and Engineering Company (Anon., 1981; Goldstein, 1983; Sartoriand Savage, 1983). These absorbents, some of which are not alkanolamines, use steric hinderancetocontrol the CO_2/amine reaction. Several different solutions are offered under the general name of Flexsorb solvents.

Table 1.4 presents the advantages and disadvantages of different alkanolamines commonly employed for the removal of acid gas constituents from gas streams.

Table 1.4 Comparisons of various alkanolamines

Monoethanolamine (MEA)

Advantages

- At moderate concentrations (on weight basis) the low molecular weight of MEA results in high solution capacity.
- High alkalinity
- Comparative ease with which it can be reclaimed from the polluted solution

Disadvantages

- Selective absorption of H_2S from gas streams comprising both H_2S and CO_2 is not possible.
- The formation of irreversible reaction products with COS and CS_2 causes excessive chemical losses if the gas contains significant amounts of these compounds.
- The MEA solution is more corrosive than solution of most other amines, particularly if the amine concentration exceeds 20% and the solution are highly loaded with acid gas.
- High heat of reaction with H_2S and CO_2 (about 30% higher than DEA for both acid gases) leads to higher energy requirements for stripping.

Diethanolamine (DEA)

Advantages

- Secondary amine like DEA are much less reactive with COS and CS_2 than primary amines. Therefore, it is the better choice for treating gas streams containing appreciable amounts of COS and CS_2.
- The low vapor pressure of DEA makes it suitable for low-pressure operations as vaporization loses are quite negligible.
- DEA solutions are less corrosive than MEA solution.

Disadvantages

- The reclaiming of contaminated DEA solution may require vacuum distillation.
- DEA undergoes numerous irreversible reactions with CO_2 forming corrosive degradation products, and for that reason, it may not be the optimum choice for treating gases with a high CO_2 content.

Methyldiethanolamine (MDEA)

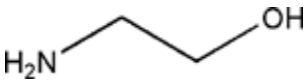
Advantages

- Selectively absorb H_2S from gas streams containing both H_2S and CO_2.
- Energy saving because of lower desorption temperature and lower heat of reaction compared to MEA and DEA.
- Less corrosive than MEA and DEA
- Because of low vapor pressure, MDEA can be used in concentration up to 60 wt% in aqueous solutions without appreciable amount of evaporation loses.

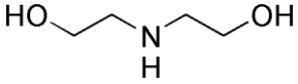
Disadvantages

- The cost of MDEA, which is higher than the other amines, has prevented its use.

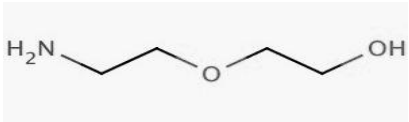
Structural formulas for the alkanolamines formerly stated are presented in Fig. 1.1. Each has at least one hydroxyl group and one amino group. In general, it can be considered that the hydroxyl group helps to reduce the vapor pressure and increase the water solubility.While the aminogroup offers the essential alkalinity in water solutions to root theabsorption of acidic gases.



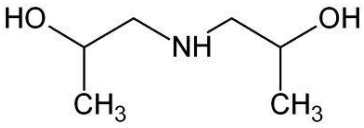
Monoethanolamine (MEA)



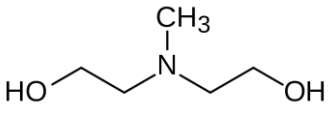
Diethanolamine (DEA)



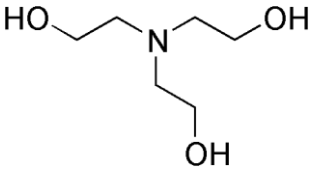
2-(2-aminoethoxy) Ethanol



Diisopropanolamine (DIPA)



Methayldiethanolamine (MDEA)



Triethanolamine (TEA)

Figure 1.1 Structural Formulas of Different Alkanolamines

The basic chemical reactions involved in this process are depicted below using a primary amine, RNH_2 (Scheme 1.2).

Reactions with H_2S:

Sulfide formation: $\mathbf{2RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S}$

Hydrosulfide formation: $\boldsymbol{RNH_2 + H_2S \rightleftharpoons RNH_3SH}$

Reactions with CO_2:

Carbonate formation: $\boldsymbol{2RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3}$

Bicarbonate formation: $\boldsymbol{RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3CO_3H}$

Carbamate formation: $\boldsymbol{2RNH_2 + CO_2 \rightleftharpoons RNH - CO - ONH_3R}$

Scheme 1.2

The basic flow diagram of amine-based acid gas removal process is shown in Fig. 1.2. Treatment with alkanolamines includes circulating gas stream upward through the absorber, countercurrent to the stream of aqueous alkanolamine solution. The rich solution from the bottom most of the absorber is heated by heat exchange with thin solution from bottom of the stripping column and is then fed to the stripping column where the absorbed gases are stripped off from the alkanolamine solution. The renewed alkanolamine is then recycled to the absorber. The concentrated hydrogen sulfide off gas obtained from the top of the stripping column is then subjected to retrieval or dumping.

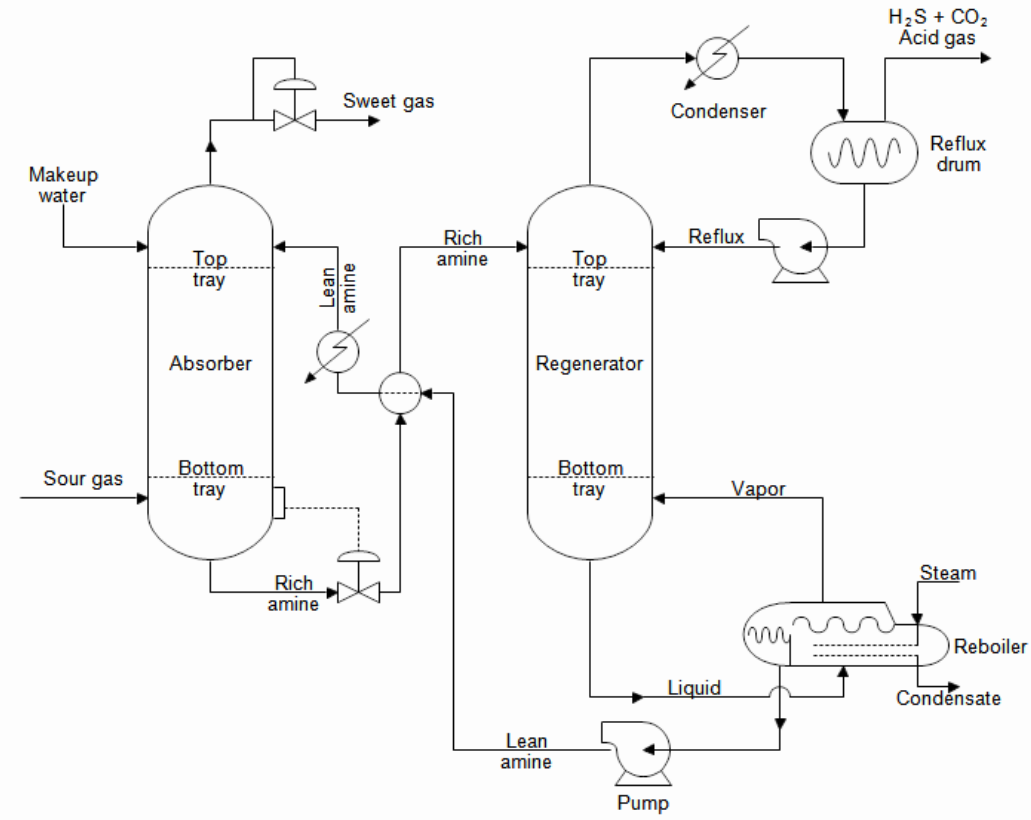


Figure 1.2 Process Flow Diagram of typical Amine-treating process used in industrial plant

1.4 Methods of Sulfur Retrieval of H_2S

1.4.1 Claus Process

H_2S should be altered into non-poisonous and better utility sulfur because of its obnoxious nature at most of the locations. The choice of process is the Claus Sulfur Recovery process. The Claus process was first patented in 1883 by the scientist Carl Friedrich Claus, the Claus process has become the industry standard. The multi-step Claus process recovers

sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the byproduct gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The byproduct gases mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants. These byproduct gases may also comprise hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia.

Explanation of the Claus Sulfur Recovery Process

H_2S gas separated from the host gas stream using amine extraction is fed to the Claus unit (Fig. 1.3), where it is converted in two steps:

1. **Thermal Step.** The H_2S-laden gas reacts in a substoichiometric combustion with air. This is done in a reaction furnace at high temperatures (1000 - 1400 ^{o}C). Claus gases (acid gas) with no further combustible contents apart from H_2S are burned in burner by the following chemical reaction:

$$2\,H_2S + 3\,O_2 \rightleftharpoons 2\,SO_2 + 2\,H_2O \quad (\Delta H = -4147.2\ \text{kJ/mol})$$

This is a strongly exothermic free-flame total oxidation of H_2S producing sulfur dioxide that reacts away in succeeding reactions. The most important one is the Claus reaction:

$$2\,H_2S + SO_2 \rightleftharpoons 3\,S + 2\,H_2O$$

The overall equation is:

$$10\,H_2S + 5\,O_2 \rightleftharpoons 2\,H_2S + SO_2 + \frac{7}{2}S_2 + 8\,H_2O$$

Showing that in the thermal step alone two-thirds of the hydrogen sulfide is converted to sulfur.The air to the acid gas ratio is controlled such that in total 1/3 of all hydrogen sulfide (H_2S) is converted to SO_2. This ensures a stoichiometric reaction for the Claus reaction in the second catalytic step. The sulfur forms in the thermal phase as highly reactive S_2 diradicals which combine exclusively to the S_8 allotrope:

$$4S_2 \rightarrow S_8$$

Side reactions

Other chemical processes taking place in the thermal step of the Claus reaction are:

The formation of hydrogen gas:

$$2\ H_2S \rightarrow\ S_2\ +\ 2H_2$$ (endothermic reaction)

$$CH_4 + 2\ H_2O \rightarrow\ CO_2\ +\ 4H_2$$

The formation of carbonyl sulfide:

$$H_2S + CO_2 \rightarrow\ S = C = O + H_2O$$

The formation of carbon sulfide:

$$CH_4 + 2S_2 \rightarrow\ S = C = S + 2H_2S$$

2. **Catalytic Step.** The reaction gases leaving the sulfur condenser are reheated to 200 - 350 ^{0}C and fed to the series of catalytic converter and sulfur condenser where H_2S react with SO_2 to produce elemental sulfur (this sulfur can be S_6, S_7, S_8 or S_9) :

$2\ H_2S + SO_2 \rightarrow 3\ S + 2\ H_2O$ (ΔH = -1165.6 kJ/mol)

Usually, the catalyst used in the catalytic converter is either activated aluminum (III) or titanium (IV) oxide.

Unavoidably a small amount of H_2S remains in the tail gas. This remaining quantity, together with other trace sulfur compounds, is usually dealt with in a tail gas unit. The latter can give overall sulfur recoveries of about 99.8%. Sulfur is used for manufacturing sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is used as fertilizer and pesticide.

Nevertheless, the Claus process has a number of intrinsic disadvantages (Plummer, 1994; Plummer and Beazley, 1986; Plummer and Zimmerman, 1986). For example:

- It operates at high temperatures
- It necessitates exact process control over the ratio of oxygen to H_2S in the feed.
- The valuable hydrogen energy is lost in this process.

- It necessitates expensive pretreatment of the feed gas if CO_2 is present in high concentrations. At least a portion of the CO_2 must be removed from the byproduct gas by pretreatment before oxidizing the H_2S to maintain the efficiency of the oxidation process.
- The sulfur content of Claus process tail gas released to the atmosphere is generally too high to meet stringent environmental regulations. To comply with these regulations, it is necessary to add more Claus stages and/or employ a separate tail gas cleanup process at great expense.

Process improvement

Over the years numerousdevelopments have been made to the Claus process. Current developments include:

Super Claus: A special catalyst in the last reactor oxidizes the H_2S selectively to sulfur, avoiding formation of SO_2. Significantly higher conversions are obtained at modest cost.

Oxygen Claus: The combustion air is mixed with pure oxygen. This reduces the amount of nitrogen passing through the unit, making it possible to increase throughput.

Better Catalysts: Higher activities have been achieved with catalysts that provide higher surface areas and macroporosity.

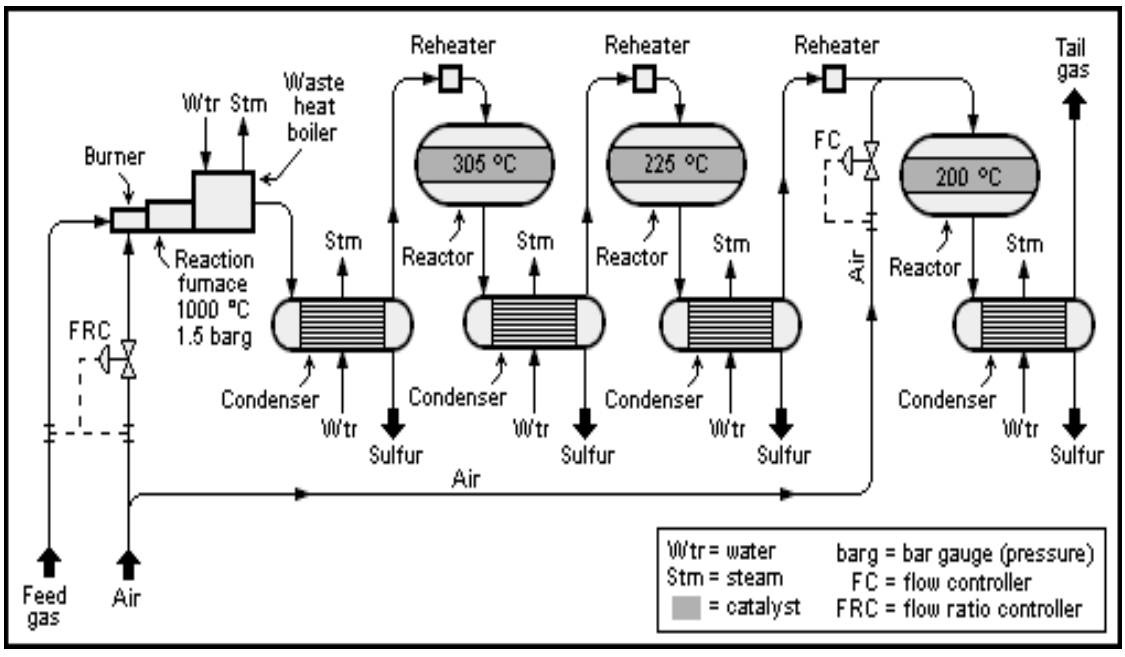


Fig 1.3: Process Flow diagram of Sulfur Recovery Process Unit

Additional Methods to Process Sour Gas

Some H_2S-containing gas is inappropriate for treatment by amine extraction because of high CO_2 levels. These streams frequently lend themselves to processing by so-called liquid redox processes such as CrystaSulf or SulFerox or ARI-LO-CAT. Instead of air, these processes use a liquid solution containing oxidized iron.

Several novel processes are being developed to make hydrogen as well as sulfur from H_2S. These are sometimes called H_2S Splitting Processes. Hydrogen is a valuable gas that is needed in oil processing and for the production of ammonia and methanol.

1.4.2. CrystaSulf

CrystaSulf is a chemical process used for removing hydrogen sulfide from natural gas, synthesis gas and gas streams in refineries and chemical plants (Department of Energy Report on Hybrid Sulfur Recovery Process for Natural Gas Upgrading, CrystaTech, Inc, Texas, US). CrystaSulf uses a liquid phase Claus reaction to convert the H_2S into elemental sulfur which is then removed from the process by filtration. This process is used in the energy industry as a one-step alternative to Amine –Claus process.

In the CrystaSulf process, a heavy hydrocarbon liquid is pumped through an absorber where the liquid associates the gas stream that contains H_2S. The H_2S is absorbed from the gas stream and the clean gas stream then exits the absorber. The H_2S remains in the liquid where it reacts with sulfur dioxide (SO_2) to form elemental sulfur and water according to the following chemical equation.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

1.4.3 Wet-oxidation LO-CAT Process

In the LO-CAT process, H_2S is converted to elemental sulfur using an ecologically safe chelated iron catalyst. The iron catalyst is detained in solution by organic chelating agents that wrap around the iron ions in a claw like fashion, preventing precipitation of either iron sulfide (FeS) or iron hydroxide ($Fe(OH)_3$). According to this process, H_2S absorbed into the slightly alkaline, aqueous LO-CAT solution (pH 8.0-8.5), is oxidized to elemental sulfur by reducing the iron ions from the ferric to the ferrous state. The reduced iron ions are then transferred from the absorber to the oxidizer where the ferrous iron is deoxidized to ferric iron by atmospheric oxygen, absorbed into the LO-CAT solution, thus renewing the catalyst.

1.5 Present Work

The current work was undertaken to develop ansubstitute process (alternative to Claus or LO-CAT process) for better consumption of H_2S present in several gas streams. The current work deals with the production of value-added chemicals utilizing the H_2S present in various byproduct gas streams obtained from different chemical industries. In accordance with the present process, value-added chemicals were produced from the H_2S-rich aqueous ammonia or alkanolamine that could be obtained from scrubbing step of the corresponding ammonia- or alkanolamine-based process. In other word, the removal of H_2S was expected to be done by conventional process. The current investigations are devoted to:

- Tri phase synthesis of value-added chemicals like dibenzyl sulfide, benzyl mercaptan, and aryl amines using the H_2S-rich aqueous ammonia and/or alkanolamines under three phase (liquid-liquid-solid) conditions in the presence of a phase transfer catalyst (PTC), Amberlite IR 400.
- Study the impact of process variables (stirring speed, catalyst loading, concentration of reactant, and temperature, alkanolamine concentration, elemental sulfur loading) on the conversions of organic reactants and selectivity of various products.
- Reusability of catalyst is also checked, which was the main advantage of using a solid catalyst over a liquid catalyst.
- Formulate an appropriate and a working mechanism or stoichiometry using the effects of various parameters on the reaction rate and conversion, to explain the course of the reaction.

1.6 Phase Transfer Catalysis

Phase Transfer Catalysis (PTC) initiates the chemical reaction between mutually insoluble reactant solutions by the addition of a transfer agent which shuttles reagents across the liquid-liquid interface. The following are the advantages of PTC:

- Its simplicity, low consumption of organic solvent and raw materials
- Faster rate under mild conditions
- use of inexpensive, recoverable and nontoxic solvents
- use of solvent-free reaction condition
- use of inexpensive and commercially available catalysts
- use of inexpensive inorganic bases for anion generation

- improvement of yield and enantioselectivity of products
- use of continuous operations for large-scale industrial applications
- improves yield, cycle time and quality of the desired product

Depending upon the physical states of the phases, PTC systems generally include liquid/liquid, liquid/solid, liquid/liquid/liquid, and gas/liquid. These systems deal with the transfer of reactant anions from an aqueous or solid phase into an organic phase. This concept extends to the transfer of cations, neutral molecules, and freeradicals and includes reactions occurring exclusively or primarily at the interface. Overall, PTC is an efficient procedure for the synthesis of a variety of compounds, such as haloalkanes, alkenes, aliphatic nitro compounds, nitriles, azides, sulfides, organometalliccompounds, pharmaceuticals, amino acids, epoxides, peptides, pesticides, and polymers. PTCs have extended its applications from research laboratories to industrial process in numerous ways.

Amongst several varieties of PTCs, many Quaternary Onium salts (quaternary ammonium, quaternary phosphonium, and quaternary arsonium salts) are used as catalysts for transferring anions in PTC reactions. Quaternary ammonium salts are generally used due to their cost and ease of availability. The standards for choosing a quaternary onium salt as a PTC catalyst comprises of extraction of the catalyst and reaction species into the organic phase and anion-activating ability, accessibility, and stability of the quaternary salt.Present study was carried out using Amberlite IR 400 as PTC.

Amberlite IR 400 is a resin-bound phase transfer catalyst and it is also one kind of Insoluble Catalyst(IC). ICs offer an important advantage of simple catalyst removal by filtration or centrifugation after the completion of a PTC reaction. Regen demonstrated that quaternary onium cations chemically bound to insoluble resins could act as PTC catalysts and suggested the term “tri-phase catalysis” (TP) to describe the related PTC reactions.

Resin-Bound Phase Transfer Catalysts:

Tomoi and Ford suggested the term‘‘polymer-supported’’ PTC to describe the PTC reactions occurring within the polymer phase. Resin-bound PTC catalysts include polymer-NR_3^+, -PPh_3^+, -SR_2^+, -crown ether, -cryptand, -azacrown, -PEG, etc. In contrast to ordinary PTC reactions using solublecatalysts, PTC reactions using resin-bound catalysts require that both reactants diffuse to active PTC sites or the resin surface or to active sites inside the resin

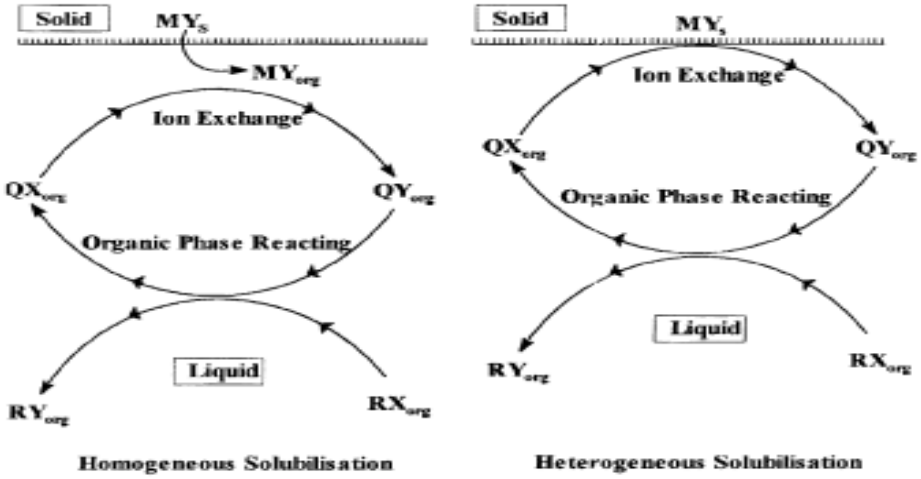
bulk phase forthe intrinsic reaction rate limited reactions. These also imply that both reactants arerequired to diffuse and penetrate the stagnant outer layer of the liquid(s) (i.e., the Nernst layer) coating the resin particle as demonstrated by Tomoi and Ford (1981), known to have a slow intrinsic reaction rate, catalyzed by thestyrene–divinylbenzene resin-bound tributylphosphonium catalyst. The resin-boundPTC catalysts generally consist of three elements, namely, the insoluble supportingcross-linked resin backbone, a spacer chain (optional), and the PTC functional group. Taking advantage of the huge amount of available ion-exchange resins, most publishedstudies on resin-bound PTC reactions use styrene–divinylbenzene resins and related resins.

1.6.1 Interfacial Mechanism of Phase-Transfer Catalysis

As the chemical reactants resides in immiscible phases, phase transfer catalysts (PTC) have the ability to carry one of the reactants as a highly active species for penetrating the interface, into the other phase where the reaction takes place, and to give high conversion and selectivity for the desired product under mild reaction conditions. This type of reaction was termed ‘‘phase-transfer catalysis’’ (PTC) by Starks in 1971. Since then, numerous efforts have been devoted to the investigation of the applications, reaction mechanisms, and kinetics of PTC. Nowadays, PTC becomes an important choice inorganic synthesis and is widely applied in the manufacturing processes of specialty chemicals, such as pharmaceuticals, dyes, perfumes, additives for lubricants, pesticides, and monomers for polymer synthesis. The global usage of PT catalysts was estimated at overone million pounds in 1996, and PTC in industrial utilization is continuously growing at an annual rate of 10–20% (Starks et al. 1994, pp 10-18). PTC is a very effective tool in many types of reactions, e.g., alkylation, oxidation, reduction, addition, hydrolysis, etherification, esterification, carbene, and chiral reactions (Starks 1997).

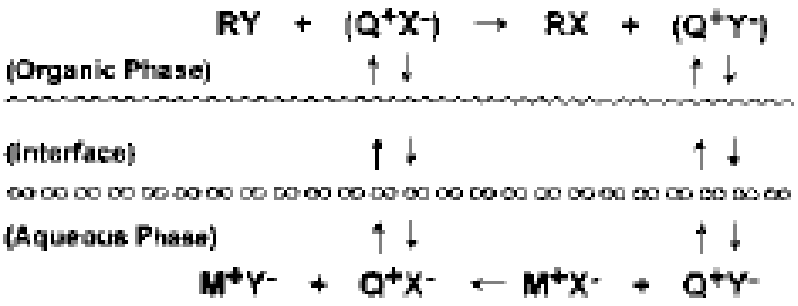
Two mechanisms (Scheme 1.3) are proposed for solid-liquid phase transfer catalysis (Starks and Liotta, 1978; Yadav and Sharma, 1981; Melville and Goddard, 1988; Naik and Doraiswamy, 1997). One of these mechanisms is applicable for conditions where the inorganic salt holds substantial solubility in the solvent and the catalyst is incapable to approach the solid surface closely. The second mechanism operates in cases where the inorganic salt is insoluble or very slightly soluble in the organic solvent and the quaternary catalyst can react directly with the solid surface to render the anionic species soluble. These

phenomena are also referred to as homogeneous and heterogeneous solubilization (Melville and Goddard, 1988). A small quantity of aqueous phase in a solid (inorganic)-organic liquid phase leads to enhancements in reaction rates and this is termed as the omega phase.

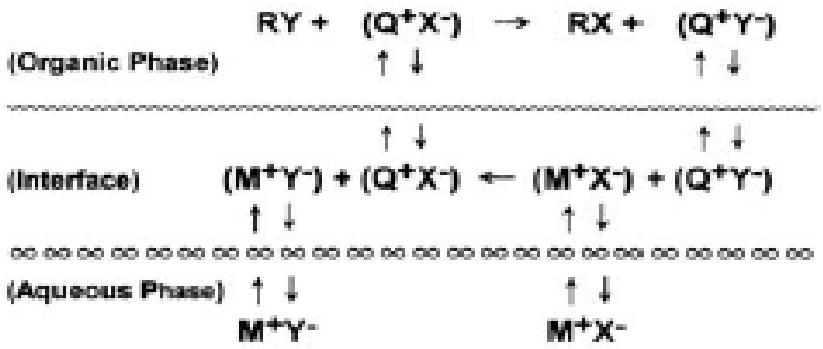


Scheme 1.3. Two distinct mechanisms for Solid-Liquid Phase Transfer Catalysis (a) Heterogeneous and (b) Homogeneous solubilization.

Two mechanisms, interfacial and extraction, are commonly used to clarify the liquid-liquid phase transfer catalysis based on the lipophilicity of the quaternary cation. The extraction mechanism (Scheme 1.4), as suggested by Starks (1971), and by Starks and Liotta (1978), is applicable to catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phase, such as benzyltriethylammonium, dodecyltrimethylammonium, and tetrabutylammonium salts. In the interfacial model, catalysts such as tetrahexylammonium and trioctylmethylammonium salts remain entirely in the organic phase because of their high lipophilicity, and exchange anions across the liquid-liquid interface (Dehmlow and Dehmlow, 1983).



Scheme 1.4. Schematic representation of Starks extraction mechanism for simple phase-transfer catalyzed displacement reaction.



Scheme 1.5. Schematic representation of Brandstrom-Starks extraction mechanism for simple phase-transfer-catalyzed displacement reaction.

In liquid-liquid-solid phase transfer catalysis (L-L-S PTC), the solid phase is the main reaction phase. The advantages of L-L-S PTC over normal PTC are: (i) increase in reaction rates by orders of magnitude; (ii) easier catalyst recovery and reuse; (iii) the reaction can be carried out in a continuous reactor by continuously separating the catalyst; (iv) better selectivity, hence the attendant difficulties of reduced activity and mechanical strength associated with liquid-liquid-solid (L-L-S) PTC can be avoided.

However, the disadvantages of L-L-L PTC are: (i) more amount of catalyst is required, which is expensive; (ii) the method is not applicable for systems where a very high temperature is required to carry out the reaction. As the temperature increases, the stability of third liquid phase decreases. However, if the catalyst is stable, then by lowering the temperature at the end of the reaction it could be easily separated into a third phase for recovery and reuse.

L-L-S PTC also named as "tri phase catalysis" as a development to PTC includes the use of a supported catalyst with two immiscible liquid-phase reagents (G.D. Yadav and P.M. Bisht, 2004).Polymer-supported ammonium salts, phosphonium salts, macrocyclicpolyethers, polar solvent residues and/or polyethylene glycols are effective and reusable phase transfer catalysts. Most of the work was reported with quaternary salts supported on polymeric supports preferably polystyrene-based matrix cross linked divinylbenzene (DVB). Usually in L–L–S PTC, the organic phase and the solid catalyst are dispersed in the continuous aqueous phase. This method holds several advantages such as easy recovery from reaction mixture by filtration, potential use in continuous flow reactors and recycling of catalyst.

The disadvantages of L–L–S PTC are higher initial cost of preparation and lower catalytic activity due to diffusion limitations. The polymer-supported catalysts are generally prepared by two methods, namely, chemical modifications of cross-linked polymer supports, and copolymerization of functional monomers with cross-linkers. The microporous resins have low specific surface areas and the polymeric chains shrink in a dry state or poor solvents. Resins swell well in good solvents to extend the polymeric chains. The macroporous resins have high specific surface areas and hardly swell in any solvent. In order to overcome the diffusion limitations, spacer chains are provided on the support and this technique leads to enhanced activity. Therefore, the overall rate in L–L–S PTC is determined by one or more of the following rate controlling processes (i) mass transfer of reactants (substrate and reagent), (ii) intra-particle diffusion of reactants, and (iii) the intrinsic rate at the active site.

The wetting nature of support matters a great deal in L–L–S PTC (G.D. Yadav and S.S. Naik, 2004). The microporous resins have low specific surface areas and the polymeric chains shrink in a dry state or poor solvents. A macroporous polymer possessing high porosity which swells considerably would be a better choice as support for the PTC.

1.6.2 Liquid-Liquid-Solid Phase Transfer Catalysis

Liquid-liquid phase transfer catalysis (LLPTC) is the most widely synthesized method for solving the problem of the mutual insolubility of nonpolar and ionic compounds (Dehmlow 1993, Starks et al. 1994, Weber and Gokel 1977, Halpern 1997 and Goldberg 1992). Two compounds in immiscible phases are able to react because of the PT catalyst. However, processes using a two phase PT-catalytic reaction always encounter the separation problem of purifying thefinal product from the catalyst. Regen (1975) first used a solid-phase catalyst (triphasecatalyst (TC) or polymer-support catalyst), in which a tertiary amine was immobilized on a polymer support, in the reaction of an organic reactant and an aqueous reactant. From the industrial application point of view, the supported catalyst can be easily separated from the final product and the unreacted reactants simply by filtration or centrifugation. In addition, either the plug flow reactor (PFR) or the continuous stirred tank reactor (CSTR) can be used to carry out the reaction. The most synthetic methods used for triphase catalysis were studied by Regen and Beese (1975-79) and Tomoi and coworkers

(1981-83). Another advantage of triphase catalysis is that it can be easily adapted to continuous processes was studied by Ragaini et al. (1986-90). Therefore, triphase catalysis possesses high potential in industrial scale applications for synthesizing organic chemicals from two immiscible reactants.

Quaternary onium salts, crown ethers, cryptands, and polyethylene glycol have all been immobilized on various kinds of supports, including polymers (most commonly methylstyrene-co-styrene resin cross-linked with divinylbenzene), alumina, silica gel, clays, and zeolites. Because of diffusional limitations and high cost, the industrial applications of immobilized catalysis (triphase catalysis) are not fully utilized. This unfortunate lack of technology for industrial scale-up of triphase catalysis is mainly due to a lack of understanding of the complex interactions between the three phases involved in such a system. In addition to the support macrostructure, the support microenvironment is also crucial in triphase catalysis since it determines the interactions of the aqueous and the organic phases with the PT catalyst immobilized on the support surface studied by Naik and Doraiswamy (1998). However, to date, few papers have discussed the microenvironment. The effect of the internal molecularstructure of the polymer support, which plays an important role in the imbibed composition, on the reaction rate has seldom been discussed. In addition to the reactivity, for a TC in an organic and aqueous solution the volume swelling, imbibed different solvent ratio, amount of active site, and mechanical structure of the catalyst must be considered. Hence, these complex interactions in the microenvironment must be solved in order to obtain a high reactivity of TC.

1.6.3 Mechanism of LLSPTC

In general, the reaction mechanism of the fluid–solid reactions involves: (1) mass transfer of reactants from the bulk solution to the surface of the catalyst pellet, (2) diffusion of reactant to the interior of the catalyst pellet (active site) through pores, and (3) intrinsicreaction of reactant with active sites. Triphase catalysis is more complicated than traditional heterogeneous catalysis, because it involves not merely diffusion of a single gaseousor liquid phase into the solid catalyst. Both organic reactant and aqueous reactant existwithin the pores of the polymer pellet. For step (3), a substitution reaction in the organicphase and an ion-exchange reaction in the aqueous phase occurred. Diffusion of both

the aqueous and organic phases within the solid support is important and various mechanismshave been proposed for triphase catalysis. However, each mechanism can only explain asingle reaction system. Naik and Doraiswamy (1998) discussed these mechanisms in their review paper.

Tundo and Venturello (1979-82) proposed a mechanism for a TC system using silicagel as support to account for the active participation of the gel by adsorption of reagents.Telford et al. (1986) suggested an alternation shell model that requires periodical changes inthe liquid phase filling the pores of the catalyst. Schlunt and Chau (1986) from the same research group tried to validate this model using a novel cyclic slurry reactor, and indicatedthat only the catalyst in a thin shell near the particle surface was utilized. Tomoi and Ford (1981) and Hradil et al. (1988) reported that a realistic mechanism involves the collision ofdroplets of the organic phase with solid catalyst particles dispersed in a continuous aqueousphase. Svec's model (1988) for transport of the organic reagent from the bulk phase throughwater to the catalyst particle has been developed in terms of emulsion polymerization.

Because the triphase reaction involves not merely diffusion of a single phaseinto thesolid support, the organic reaction take places in the organic phase and the ion-exchange reaction occurs in the aqueous phase. The catalyst support is usually lipophilic. The organic phase and aqueous phase fill the catalyst pores to form the continuous phaseand the disperse phase, respectively. The interaction between quaternary salts as well asthe organic phase and aqueous phase play a crucial role in promoting the triphase reaction rate.

CHAPTER 2

LITERATURE STUDY

Chapter 2

Literature Study

Abstract

This chapter deals with the literature study associated to the use of alkanolamines as H_2S gas absorbent, Different methods of synthesizing Benzyl mercaptan and Dibenzyl sulfide, Use of various catalyst for the development of valuable products using the H_2S present in gases.

2.1 Use of Aqueous Alkanolamines for the Removal of H_2S

As discussed in preceding Chapter 1, hydrogen sulfide (H_2S) removal and retrieval from the gas streams by ammonium hydroxide are well documented by Kohl and Nielsen, 1997. This process was established by Hamblin, 1973 for removal of H_2S from gas streams using ammonium hydroxide to produce ammonium hydrosulfide, which was further oxidized by an air stream to get an effluent stream containing ammonium polysulfide and treating the ammonium polysulfide containing stream to recover elemental sulfur. In recent times, Asai et al. (1989) studied the rates of simultaneous absorption of H_2S and ammonia into water in an agitated vessel with a flat interface and Rumpf et al. (1999) studied the simultaneous solubility of ammonia and H_2S in water at temperatures from 313 to 393 K and total pressures up to 0.7 MPa.

In contrast, aqueous alkanolamines are now-a-days extensively used in industry for the removal of H_2S from gas streams as deliberated in Chapter 1. Lot of research works is also dedicated to the study on the equilibrium solubility of pure H_2S, mixture of acid gases (H_2S and CO_2), and the mathematical representation of the experimental solubility data for H_2S, CO_2 and their mixture using various alkanolamines (Lee et al., 1976; Lawson and Garst, 1976; Isaacs et al., 1980; Austgen et al., 1989; Weiland et al., 1993; Kaewsichan et al., 2001; Al-Baghli et al., 2001; Sidi-Boumedine et al., 2004; Vallée et al., 1999).

2.2 Preparation of Benzyl Mercaptan

Benzyl Mercaptan (BM) is useful as a raw material for the synthesis of herbicides in the thiocarbamate family (Labat, 1989). It is predominantly used for the synthesis of herbicides like esprocarb, prosulfocarb, tiocarbazil, etc. Preparation of BM from benzyl chloride using sodium hydrosulfide and ammonium hydrosulfide reagents is well documented.

As for example, Hoffman and Reid (1923) prepared BM by reacting benzyl chloride with ethanolic solution of molten sodium sulfide (melted at 90 ^{0}C) saturated with H_2S. The mixture was allowed to stand in the cold, with frequent shaking for 4 days.

Heather (1988) prepared BM by reacting benzyl chloride with sodium hydrosulfide in the two-phase conditions under H_2S atmosphere at a temperature of about 50^{0}C until approximately 90% of the starting material was converted to the BM (stirred for about 5 hours), then temperature was elevated to about 80 ^{0}C for the balance of the reaction (stirred for an additional 1.5 hours).

Bittell and Speier (1978) prepared BM by using a solution of NH_3 and methanol saturated with H_2S at 0 ^{0}C. Benzyl chloride was added to this methanolic ammonium hydrosulfide (NH_4SH) solution at 0 ^{0}C while H_2S is slowly bubbled through the solution. The reaction was completed in 1 hour with BM (92%) and DBS (8%) as the detectable products.

Labat (1989) prepared BM of more than 99% purity by reacting benzyl chloride and ammonium hydrosulfide in a molar ratio $NH_4SH/C_6H_5CH_2Cl$ of at least 1, preferably between about 1.05 and 1.5 under autogenous pressure in a closed reactor in two steps. The first step comprised adding benzyl chloride to an aqueous hydrosulfide at a temperature below 80^{0}C. The second step involved heating the reaction mixture to a temperature in the range of 80-100^{0}C for about 2 hours.

BM was also prepared from the corresponding thioacetates via Pd-catalyzed methanolysis with borohydride exchange resin (Choi and Yoon, 1995a) and from the corresponding alkyl halides and epoxides using hydrosulfide exchange resin in methanol in the presence of equimolar amounts of triethylammonium chloride (Choi and Yoon, 1995b).

2.3 Preparation of Dibenzyl Sulfide

Dibenzyl sulfide (DBS) is havingmany applications such as additives for extreme pressure lubricants, anti-wear additives for motor oils, stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations (Pradhan and Sharma, 1990). DBS can also be oxidized to prepare some useful synthetic intermediates like dibenzylsulfoxide and dibenzylsulfone (Varma et al., 1997; Mohammadpoor-Baltork et al., 2005).

Pradhan and Sharma (1990) synthesized DBS and bis (*p*-chlorobenzyl) sulfide by reacting the respective chlorides with sodium sulfide using different phase transfer catalysts (PTC) under liquid-liquid and solid-liquid mode. Tetrabutylammonium bromide (TBAB) was found to be the most effective out of the six catalysts they tried under solid-liquid mode of operation. A detailed study was performed using the best catalyst, TBAB.

Recently, Ido et al. (2000) investigated the property of third phase that affects the reaction rate of benzyl chloride with sodium sulfide in the presence of tetrahexylammonium bromide as a PTC.

Pradhan and Sharma (1992b) also studied the kinetics of preparation of DBS and bis (4-chlorobenzyl) sulfide under solid-liquid modes with solid sodium sulfide using easily separable unimpregnated inorganic solid catalyst like basic alumina and Amberlyst A27 (Cl^- form) anion exchange resins.

Preparations of DBS using various types of reagent and starting material are also well documented. For examples, Bandgar et al. (2000) prepared symmetrical sulfides including DBS from the corresponding halides using polymer supported sulfide anion. Lakouraj et al. (2002)

and Movassagh and Mossadegh (2004a, 2004b) prepared DBS by the reduction of corresponding disulfide using zinc powder in the presence of $AlCl_3$ in aqueous media. DBS was also prepared by the deoxygenation of corresponding sulfoxide using various reducing agents like Al-$NiCl_2$-$6H_2O$ (Raju et al., 2005), 1,3-dithiane in the presence of catalytic amounts of N-bromosuccinimide, 2,4,4,6-tetrabromo-2, 5-cyclohexadienone or Br_2 as the source of electrophilic bromine (Iranpoor et al., 2002), and 2,6-Dihydroxypyridine in refluxing acetonitrile (Miller et al., 2000). However, the reduction of sulfoxides with these compounds sometimes suffer from serious disadvantages, such as use of an expensive reagent, difficult workup procedures, harsh acidic conditions, very high reaction temperatures and long reaction times (Iranpoor et al., 2002). In addition, the preparation of DBS by the reduction of corresponding sulfoxide is impractical as sulfoxide itself is usually prepared by the oxidation of the sulfide.

The kinetics of reduction of nitrotoleunes by aqueous ammonium sulfide under LL PTC with the use of (TBAB) as PTC was also studied (Narayan CPradhan, Anand V Patwardhan, Sunil K Maity, 2006). The reaction of benzyl chloride with ammonium sulfide under LL PTC using TBAB as PTC was also studied.

DBS was synthesized by reacting benzyl chloride and aqueous ammonium sulphide using TBAB as phase transfer catalyst. The parametric study was done on the selectivity of DBS. It was found that DBS can be selectively prepared by keeping high benzyl chloride concentration, High NH_3/H_2S ratio (SujitSen, Patwardhan, S K Maity, N C Pradhan, 2007).

The reaction of BC with H_2S rich MEA solution under L-L PTC was studied by SujitSen, N.C.Pradhan and Patwardhan (2010). It was found that higher ratio of MEA/H_2S favored the formation Dibenzyl sulfide and if the ratio is lower it favors the formation of benzyl mercaptan. TBAB catalyst was used.

2.4 Use of Tri Phase Catalyst

In the L-L PTC the catalyst was found to be soluble in both the phases and it possesses a major problem that we do not get product in pure form. For removing the dissolved catalyst it requires several water washes of the aqueous phase and treatment of the high volume of the

effluent. The separation of catalyst from the reaction mixture can be achieved by extraction, distillation and adsorption and all these are energy intensive.

Pradhan and Sharma (1992), studied the catalytic effect of basic alumina and Amberlyst A27(Cl^-) form, on the reaction of benzyl chloride and parachlorobenzyl chloride with solid sodium sulphide. The catalyst used in this case is Tri Phase catalyst.

G.D Yadav and N Kirthivasan(1997), studied the use of a novel catalyst based on heteropolyacid supported on clay, particularlydodecatungstophosphoric acid (DTP) supported on K-10 clay and they compared it with some other solid catalyst. DTP/K-10 catalyst was found to be reusable and efficient at high temperatures.

G.D Yadav and S.S Naik (2000), prepared a clay supported phase transfer catalyst and used it for the preparation of benzoic anhydride from benzoyl chloride and sodium benzoate using clay-supported quaternary ammonium salts at 30 °C They found that clay supported catalyst were more active than polymer supported catalyst. They found the selectivity to be 100%.

G.D Yadav and A.V Joshi (2001), used solid acid catalyst to synthesis tert amyl methyl ether (TAME) by reacting tert amyl alcohol and methanol. A comparison was made among different solid catalyst and Amberlyst-36 was found to be very effective.

G.D Yadav and O.V Badure (2007) studied the merits of creation of a third phase in biphasic reaction. They found that use of L-L-L PTC enhances the conversion and increase the selectivity also. He confirmed it by reacting phenol with benzyl chloride under L-L PTC and L-L-L PTC separately and comparing the data obtained.

S K Maity, Narayan C Pradhan, A V Patwardhan (2008) studied reduction of p-nitrotoluene by aqueous ammonium sulfide using serelite SRA400 a triphase catalysis reaction. The rate of reduction of PNT was established to be proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Enhancement of the rate was also observed with the once used catalyst due to the presence of elemental sulfur on the surface of the catalyst.

B Gao, Z Wang, L Wang(2010), studied the effect of different type of quaternary salt type tri phase catalyst on the esterification reaction of benzyl chloride with sodium acetate. They found that 1) Among quaternary phosphonium and quaternary ammoninum type TPC, ammonium type have the higher activity than quaternary ammonium-type catalyst, 2) TPC which is highly lipophilic, substitution takes place at N atom and theyhave higher catalytic activity, 3) TPC having longer spacer arm that links the quaternary onium salt group to the matrix microsphere, shows higher catalytic activity, 4)The hydrophilic and hydrophobic property of the TPC is affected by the bonding density of quaternary onium salt group and hence influences the catalytic activity.

2.5 Conclusion

The simultaneous absorption of H_2S and NH_3 into water (Asai et al., 1989; Rumpf et al., 1999), and the use of ammonium hydroxide (Hamblin, 1973) and aqueous alkanolamine (Kohl and Nielsen, 1997) for the removal of H_2S from gas streams are well documented. However, there is no information in the literature on the use of aqueous ammonium sulfide (or H_2S-rich aqueous alkanolamines that can be obtained from the corresponding unit) to produce any value-added chemicals.

There is no published work on the detailed kinetic study of preparation of BM from benzyl chloride using H_2S-rich aqueous alkanolamine under tri-phase conditions in the presence of a PTC. Moreover, no attempt has been made in the past to prepare DBS by the tri-phase reaction of benzyl chloride with H_2S-rich aqueous alkanolamine in the presence of anAmberlite IR 400 as PTC.

CHAPTER 3
EXPERIMENTAL

Chapter 3

Experimental

Abstract

This chapter deals with the detailed experimental procedure followed in all cases of experimental studies. It includes chemicals, equipment details, preparation of several reagents and experimental procedure.

3.1 Chemicals and Catalyst

Hydrogen sulfide (H_2S) prepared in the laboratory using Kipp's apparatus and its preparation and estimation of sulfide content in it are discussed in detail in below section. Sulfide content is estimated by iodometric titration method. Water used here is purified by deionization. Other reagents, including toluene (≥ 99.5 %) of analytical grade are acquired from Merck (India) Ltd., Mumbai. Amberlite IR 400 was procured from Merck (India) Ltd., Mumbai. Monoethanolamine (≥98 %) synthesis grade were procured from Merck (India) Ltd., Mumbai, India. Iron (II) sulfide (FeS) sticks were obtained from Sigma Aldrich, Mumbai, India. Synthesis grade benzyl chloride (≥ 99 %) was obtained from Merck (India) Limited, Mumbai, India. Also, the chemicals used for iodometric titration for the estimation of sulfide content i.e., sodium thiosulfate, potassium iodate, potassium iodide, starch powder, sulfuric acid (98 % pure) and sodium hydroxide pellets of analytical grade were procured from Merck (India) Ltd., Mumbai.

3.2Preparation of H_2S-Rich Aqueous Alkanolamines

Initially, for the preparation of H_2S-rich aqueous monoethanolamine (MEA) around 30-35 wt% aqueous alkanolamine solution was prepared first by adding a suitable quantity of desired alkanolamine in distilled water. Then H_2S gas produced in the Kipp's apparatus as shown in below fig. 3.1., was bubbled through this aqueous alkanolamines in a 250 mL. standard gas bubbler. H_2S gas was prepared in laboratory scale in Kipp's apparatus by reacting FeS sticks with H_2SO_4. The concentration of H_2SO_4 was taken as 1 molar and the reaction carried out in Kipp's apparatus is as follows:

$$FeS + H_2SO_4 \xrightarrow{exothermic\ reaction} H_2S\,(g) + FeSO_4$$

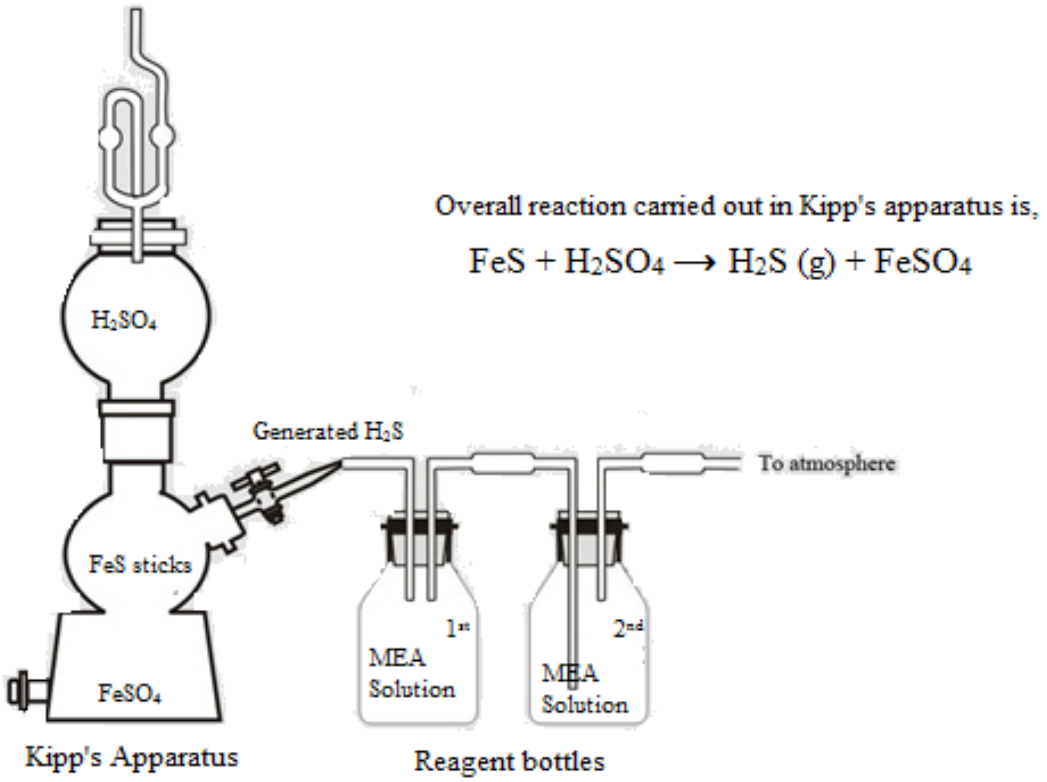


Fig. 3.1.Schematic diagram for the absorption of H_2S in MEA solution

Since the reaction of H_2S with alkanolamines is exothermic (Kohl and Nielsen, 1997), the gas bubbler containing aqueous alkanolamine was kept engrossed in an ice water bath in order to prevent the oxidation of sulfide and consequently to prevent the formation of disulfide. The unabsorbed H_2S gas from the first bubbler was sent to another bubbler containing ~ 1M MEA solution whose outlet was open to the atmosphere. Liquid samples were withdrawn from time to time after the gas bubbling was stopped and the samples were analyzed for sulfide content (Scott, 1966). The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous alkanolamines.

3.3 Apparatus and Equipment Setup

In typical experiment, all the reactions were carried out into a thermostated (± 0.5 ^{0}C) three-necked 250-ml (6.5 cm I.D.)in a batch mode equipped in a fully baffled mechanically agitated glass reactor. Borosilicate glass beaker was used as the contactor and three-necked flask, a dropping funnel serving the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the feed. A 2.0 cm-diameter six-bladed glass disk turbine impeller with the facility of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. This arrangement ensured excellent solid-liquid mixing for high mass transfer rate. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within ± 0.5 ^{0}C and mechanically stirred at a known speed with an electric motor. The schematic diagram of the experimental setup is as shown in Fig. 3.2.

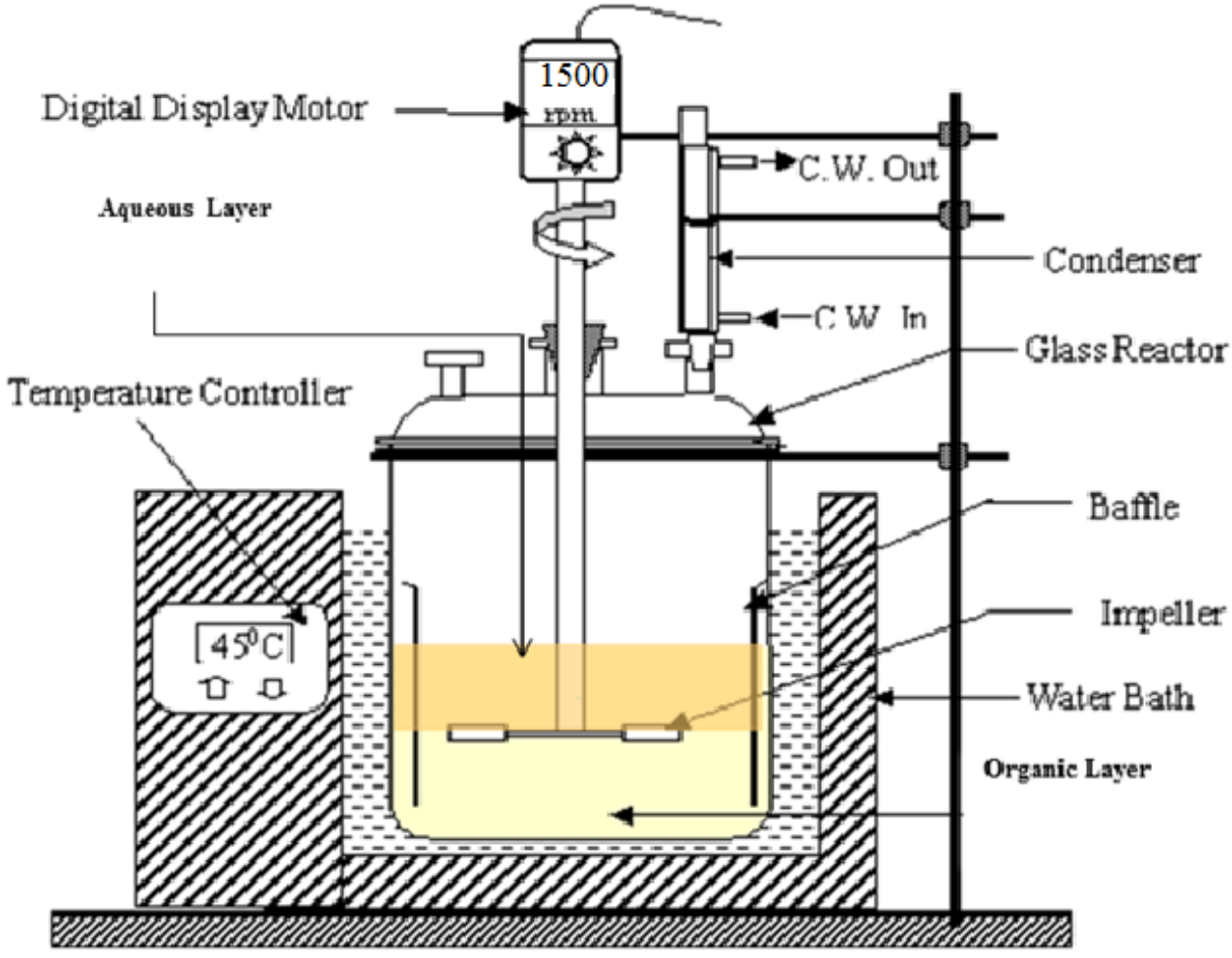


Fig. 3.2.Schematic diagram of the batch reactor assembly

3.4 Reaction Procedure

In a typical experimental run, known quantities of 50 mL of aqueous phase containing a known concentration of sulfide was charged into the three neck batch reactor and kept well agitated until the steady state temperature was reached. 50 mL of the organic phase containing measured amount of organic reactant (benzyl chloride), and phase-transfer catalyst (Amberlite IR 400) arecharged into the reactor and then dissolved in organic solvent (toluene) to form an organic solution. To start the reaction, the aqueous and organic solutions are mixed in a 250-mL flask immersed in an isothermal water bath. The reaction mixture was then agitated at a constant stirring speed. The organic phase sample about 0.1mL, of the organic layer was withdrawn at a regular time interval of 60-480 min., after stopping the agitation and allowing the phases to separate, was put into the test tubes. The sample (0.1 mL) was withdrawn periodically from the reactor and put into the glass vials.

3.5 Method of Analysis

3.5.1 Determination of Sulfide Concentration

Initial sulfide concentrations were determined by standard iodometric titration method (Scott, 1966) as given below.

Preparation of standard (0.025 M) KIO_3 solution: 4.28 gm of KIO_3 was weighed accurately and dissolved in distilled water and was made up to 1 L in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulfate solution: 25 gm of $Na_2S_2O_3.5H_2O$ crystals was weighed and dissolved in distilled water and made up to 1 L in a graduated volumetric flask with distilled water. About 0.1 g of sodium carbonate or three drops of chloroform was added to this solution to keep the solution for more than a few days.

Standardization of sodium thiosulfate solution by standard potassium iodate solution: 25 mL of 0.025M KIO_3 solution was taken and 1 gm (excess) of potassium iodide (KI) was added to it followed by 3 mL of 1 M sulfuric acid. The liberated iodine (I_2) was titrated with thiosulfate

solution. When the color of the solution became a pale yellow, it was diluted to ca. 200 mL with distilled water. 2 mL of starch solution was added, and the titration was continued until the color changed from blue to colorless. The chemical reaction involved in this titration is given below.

$$KIO_3 + 5KI + 3H_2SO_4 \rightleftharpoons 3I_2 + 3H_2O + 3K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI$$

Therefore, 1 mole of $KIO_3 \equiv 3\times2$ mole of $Na_2S_2O_3$.

$$\therefore Strength\ of\ thiosulfate\ soluton = \left(\frac{6 * strength\ of\ KIO_3 * volume\ of\ KIO_3}{volume\ of\ thiosulfate\ consmed}\right)$$

Estimation of sulfide concentration: Hydrogen sulfide and soluble sulfides can be determined by oxidation with potassium iodate in an alkaline medium. 15 mL of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 mL of sulfide solution containing about 2.5 mg of sulfide was then added to it followed by the addition 10 mL of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 mL of KI solution and 20 mL of 4M sulfuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as given by the following reaction. For sulfide solution having sufficiently high sulfide concentration, suitable dilution was made before the estimation of sulfide by above mentioned procedure.

$$4IO_3^- + 6OH^- + 3S^{2-} = 3SO_4^{2-} + 4I^- + 6H_2O$$

4 mole of IO_3^- ≡ 3 mole of S^{2-}

$$H_2S\ concentration = \left\{\left[(15 * S_{iodate}) - \frac{(V_{thiosulfate} * S_{thiosulfate})}{6}\right] * \frac{3}{4} * \frac{N_d}{10}\right\}$$

Where S_{iodate}= Strength of KIO_3

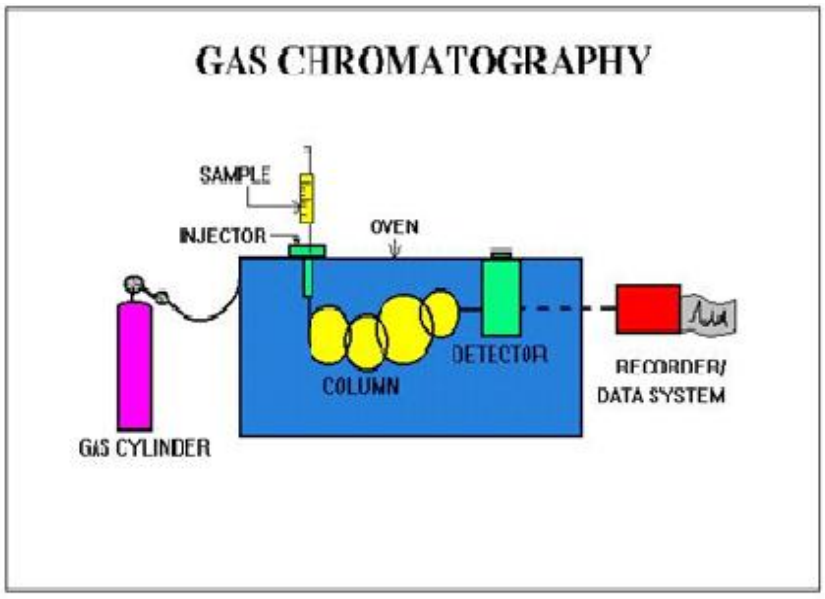
$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$= Strength of thiosulfate

N_d= Number of times of dilution

3.5.2 Analysis of Organic Phase

All samples and the contents of Dibenzyl sulfide, Benzyl mercaptan and dissolvent from the organic phase were analyzed by gas liquid chromatography (GLC). A Chemito Model 8610 GC interfaced with Shimadzu C-R6A Chromatopac Data Processor was used for the analysis.The analyzing conditions are as follows: a gas chromatography (GC-8610) with a detector, Flame Ionization Detector (FID). The column used is a 2 m × 3 mm stainless steel column packed with Chromosorb WHP (80-100 mesh), which were impregnated with 10% SE-30 was used for analysis in conjunction with a FID. Synthetic mixtures of the reactant and internal standard were used to calibrate the chromatograms and quantify the data. The optimum operation conditions of GC are the following: injection temperature, 150 ^{0}C; column temperature, 145 ^{0}C; FID temperature, 145 ^{0}C; carrier gas, nitrogen gas with a flow rate of 30 mL.min^{-1}; and sample volume, 0.5 µL during the analysis. The products formed were analyzed by comparison of their retention times with authentic samples. Yields were determined from standard curve and using acetone as internal standard. In L-L-SPTC, the sole products, Dibenzyl sulfide and Benzyl mercaptan, were confirmed by GC analysis.



Schematic diagram of Gas Chromatography

GC 8610 Gas Chromatography

CHAPTER 4

REACTION OF BENZYL CHLORIDE WITH H_2S-RICH AQUEOUS MONOETHANOLAMINE UNDER LIQUID–LIQUID-SOLID PHASE TRANSFER CATALYSIS

Chapter 4

Reaction of Benzyl Chloride with H_2S-Rich Aqueous Monoethanolamine under Liquid-Liquid-Solid Phase Transfer Catalysis

Abstract

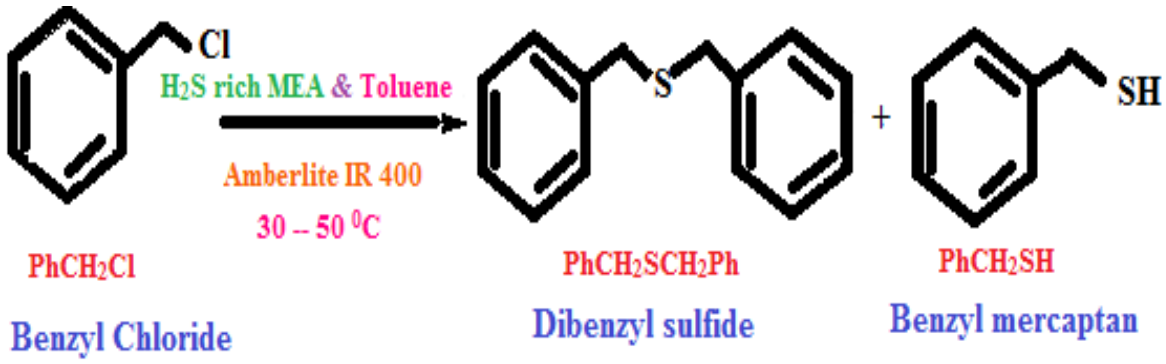
This chapter describes a detailed study for the synthesis of Dibenzyl sulfide selectively from reaction of benzyl chloride (BC) with H_2S-rich aqueous monoethanolamine under liquid-liquid-solid phase transfer catalysis (LLS-PTC).It includes parametric studies following mechanistic investigation of the process parameters to maximize BC conversion and DBS selectivity. In parametric studies, effects of temperature, catalyst concentration, BC concentration, initial sulfide concentration and MEA concentration on BC conversion and DBS selectivity were examined.

4.1 Introduction

In the present work, the reaction of benzyl chloride (BC) with H_2S-rich aqueous monoethanolamine (MEA) can give both Dibenzyl sulfide (DBS) and Benzyl mercaptan (BM) as products as per the below scheme. The commercial importance of these compounds has been mentioned in Chapter 2. In the present study, the reaction was carried out in batch mode under tri-phase conditions (liquid-liquid-solid) both in the absence and in the presence of phase transfer catalyst (PTC), namely, Amberlite IR 400. Dibenzyl sulfide (DBS) and benzyl mercaptan (BM) were detected as the products from the reaction mixture by gas liquid chromatography (GLC). Although there is a possibility of formation of benzyl alcohol by alkaline hydrolysis of benzyl chloride, it was not detected in the reaction mixture even after a batch time of 10 hrs. Accordingly, the reaction system may be represented by Scheme 4.1.

The term 'selectivity' of the two products, DBS and BM, used in this study is defined as the fraction of benzyl chloride converted to a particular product divided by the total fractional conversion of benzyl chloride. The selectivity of DBS (or BM) was maximized by changing various parameters such as stirring speed, temperature, aqueous sulfide concentration, MEA

concentration, catalyst loading and concentration of benzyl chlorideas discussed below in the respective sections. From the detailed study of effects of various parameters on the reaction, a suitable mechanism was established which could explain the course of the reaction.



Scheme 4.1

Parametric studies have been performed following one-variable-at-a-time (OVAT) approach to see the effect of various parameters such as speed of agitation, temperature, aqueous sulfide concentration, MEA concentration, catalyst loading and BC concentration on BC conversion and DBS selectivity.

4.2 Results and Discussion

4.2.1 Parametric Study

4.2.1.1 Effect of Speed of Agitation

The mass transfer as well as the chemical reaction is important in influencing the conversion on rate of the three-phase reaction. In this study, to ascertain the influence of mass transfer resistance of the reactants to the reaction phase, effect of the agitation speed on the conversion of benzyl chloride was varied in the range 1000-2500 rpm under otherwise identical experimental conditions in the presence of PTC (Amberlite IR 400), as shown in Fig. 4.1. For agitation speed over 1000 rpm, the conversion of benzyl chloride is insensitive to the agitation speed. This result is different from that of other reaction systems that require a high agitation speed to reach a constant value of conversion.

The main reason is that other reactions systems need a relatively larger interfacial area to increase the mass transfer rate. However, the active intermediate of the catalyst (Q^2S), which is hydrophobic, likes to stay in the organic phase, in which the interfacial area is not so important. As it is evident from the figure, the variation of conversion of benzyl chloride with stirring speed is so small that the mass transfer factors become unimportant and the reaction rate is controlled purely by the kinetics. Therefore, all other experiments were performed at a stirring speed of 1500 rpm in order to ensure the absence of mass transfer resistance.

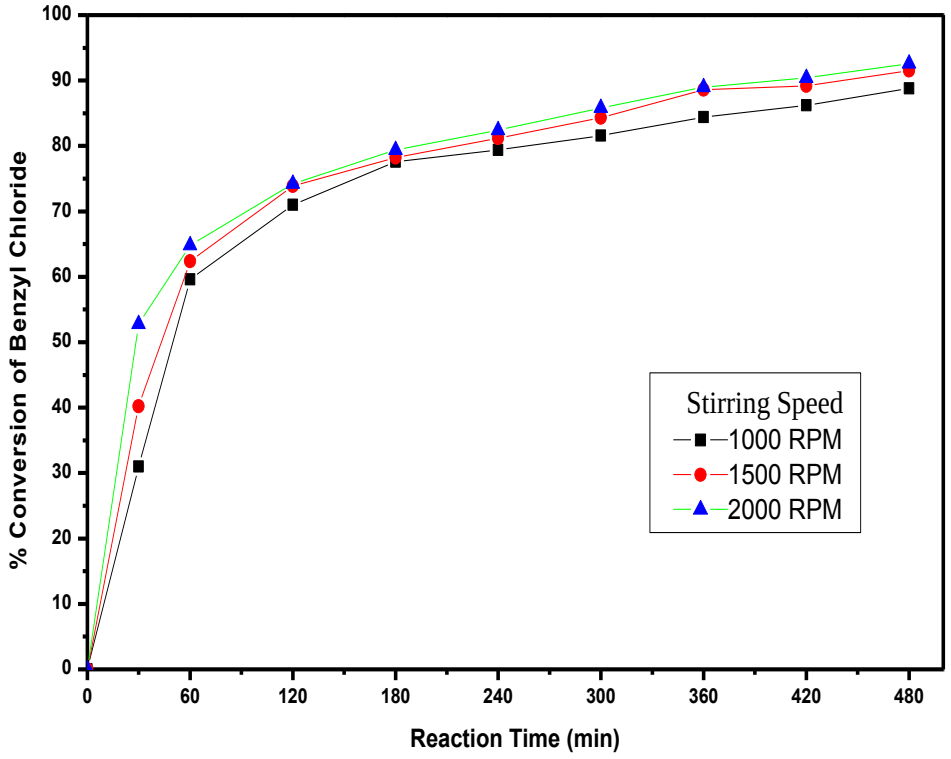


Fig. 4.1: Effect of speed of agitation on the conversion of BC.

Operating Condition: Volume of organic phase =50 ml; concentration of BC = 2.6 M org. phase; concentration of toluene = 6.6 M org. phase; volume of aqueous phase = 50 ml, concentration of catalyst = 0.1 M org. phase; concentration of sulfide = 2 M, MEA/H_2S mole ratio = 1.74; temperature = 45 ^{0}C.

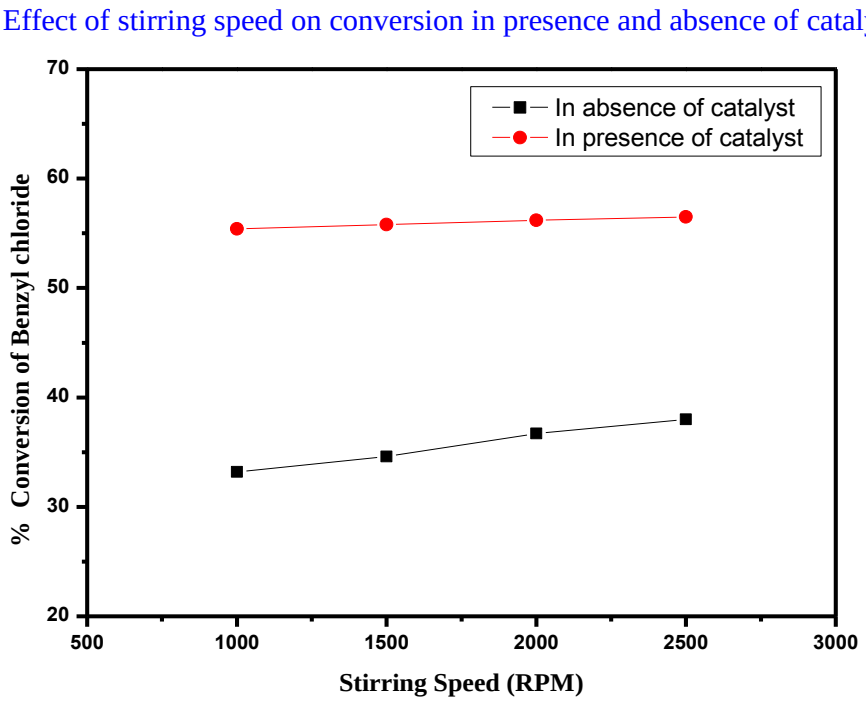


Fig. 4.2: Effect of speed of agitation onconversion of BC in presence & absence of catalyst.

$$\%ConversionofBC = \frac{initialconc. - finalconc.}{initialconc.} \times 100\%$$

$$\%SelectivityofDBS = \frac{molesofDBSformed}{molesofBCconverted} \times 100\%$$

4.2.1.2 Effect of Temperature

The present work investigates the reaction of BC with Toluene catalyzed by a new resin catalyst Amberlite IR 400 in the presence of H_2S-rich aqueous monoethanolamine under various reaction temperatures was studied under otherwise similar reaction conditions at six different temperatures in the range 30 – 55 ^{0}C. Fig. 4.3 shows the effect of temperature on conversion of benzyl chloride. As expected, the rates of most organic reactions increase with the increase in temperature from the transition-state theory. For this reason, it is considered that increasing temperature is likely to promote slow organic phase reactions in PTC system. It is obvious that the reactivity (conversion) of BC is increased with an increase in the temperature. The reason is that the number of reactant molecules, which possess larger activated energy at a higher temperature. Thus the conversion of BC is increased. The other point is that the collision of the

reactants at higher temperature is also increased. Hence, the reaction rate increases with increasing temperature.

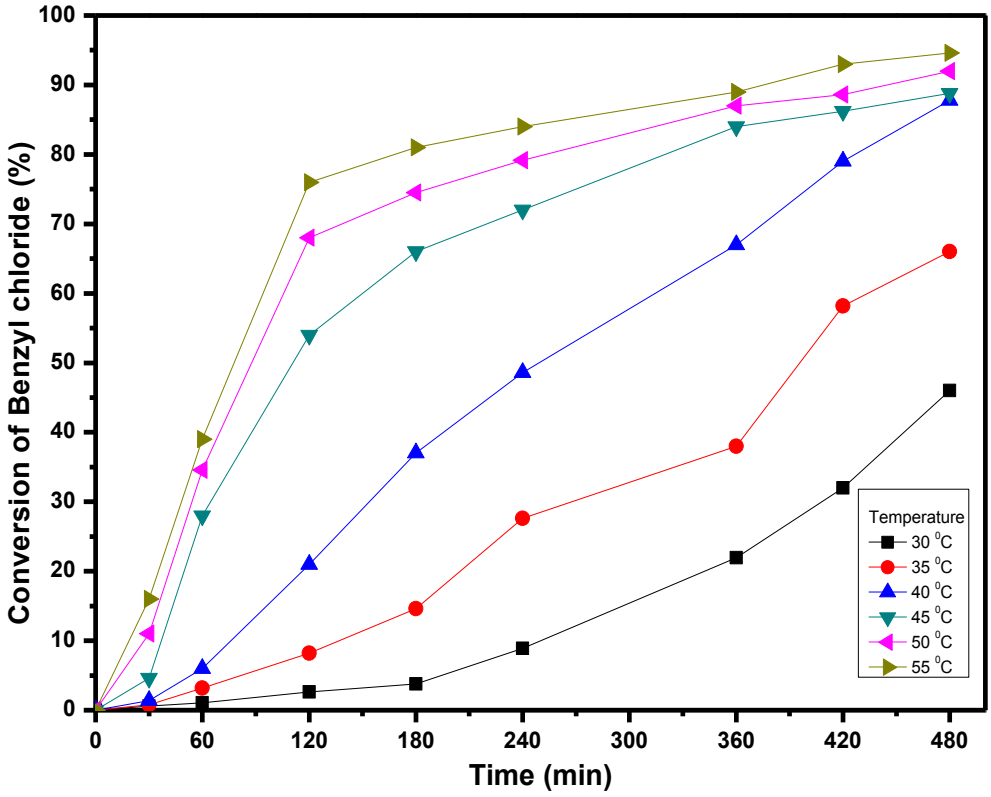


Fig. 4.3: Effect of temperature on BC conversion

Operating Condition: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Concentration of toluene = 6.6M org. phase; volume of aqueous phase = 50ml; Concentration of catalyst = 0.1M org. phase; Concentration of sulfide = 2.3M, MEA/H_2S ratio – 2.1; Stirring speed – 1500 rpm.

The effect of temperature on the selectivity of DBS is shown in Fig. 4.4. As observed from the table, the selectivity of DBS is almost unaffected by the temperature for a given conversion of benzyl chloride. Therefore, with an increase in temperature, the reaction rate increases without significantly affecting the selectivity of the products.

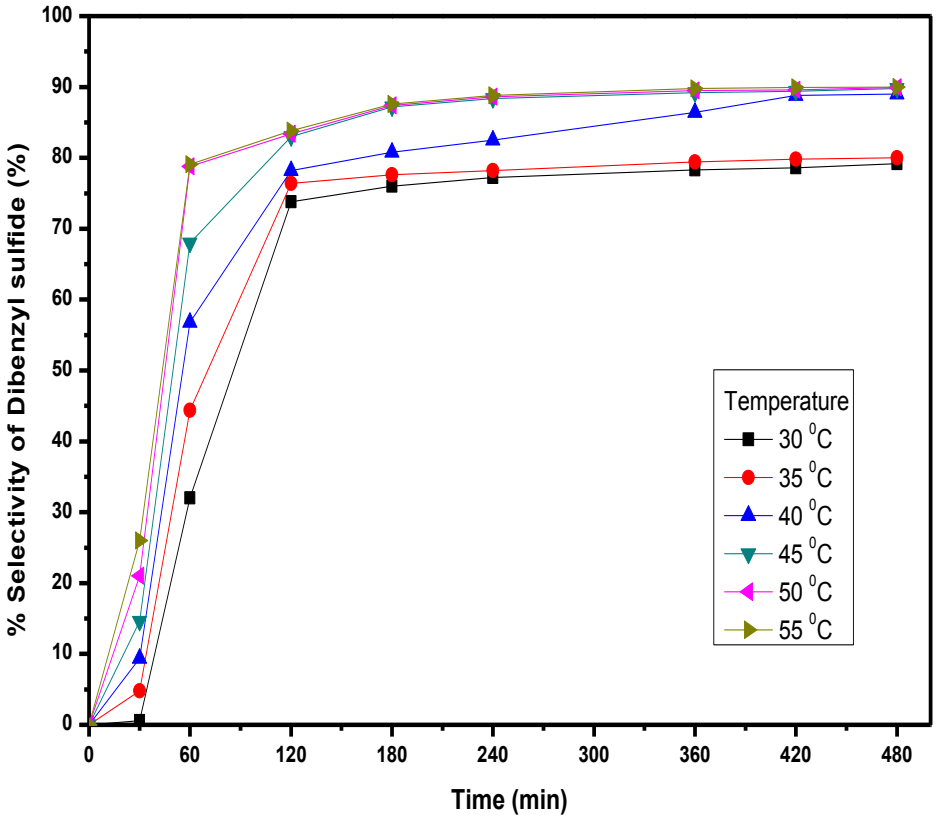


Fig. 4.4: Effect of temperature on DBS selectivity

Operating Condition: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Concentration of toluene = 6.6M org. phase; volume of aqueous phase = 50ml; Concentration of catalyst = 0.1M org. phase; Concentration of sulfide = 2.3M, MEA/H_2S ratio – 2.1; Stirring speed – 1500 rpm.

Initial rate of reaction of benzyl chloride was calculated at different temperatures and an Arrhenius plot of –ln (initial rate) versus 1/T was made as shown in Fig. 4.5 and Fig. 4.6. The apparent activation energy for the reaction of benzyl chloride was calculated from the slope of the straight line as 40.7 KJ mol^{-1}. The observed high apparent activation energy again confirms the fact that the reaction is kinetically controlled.

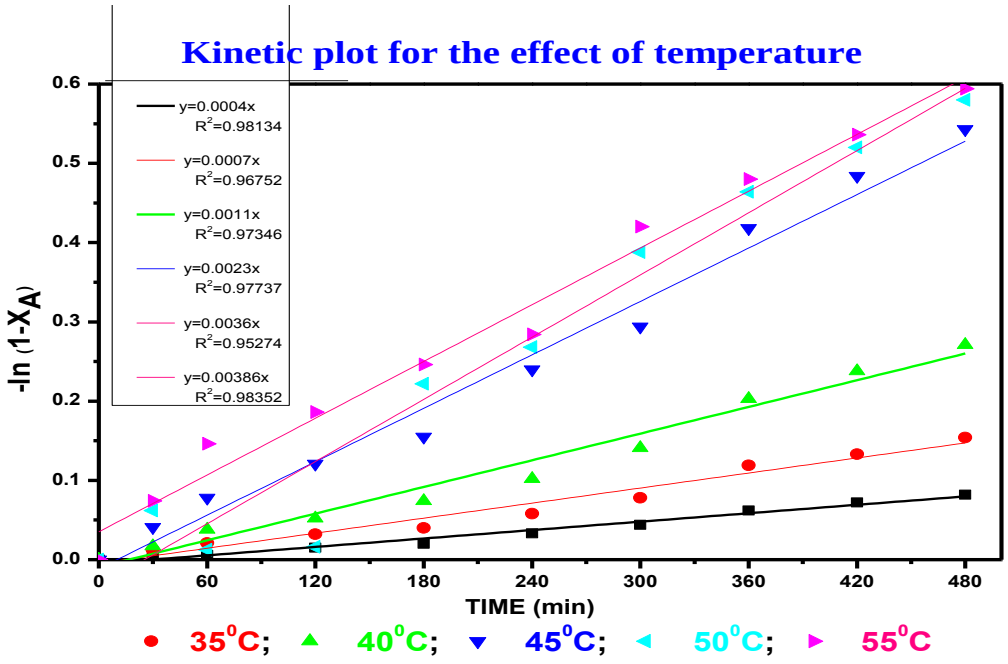


Fig. 4.5: Kinetic plot for the effect of temperature

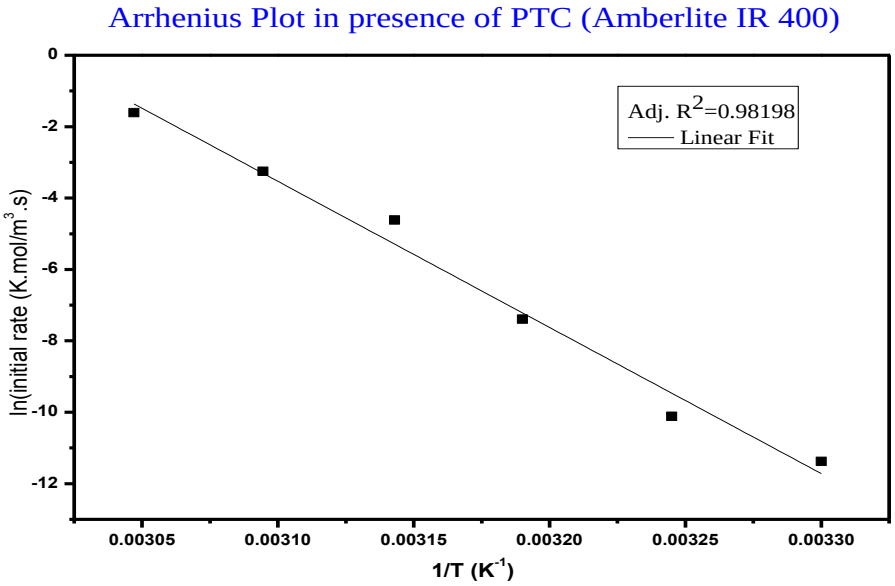


Fig. 4.6: Arrhenius plot for activation energy

Operating Condition :Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Concentration of toluene = 6.6M org. phase; volume of aqueous phase = 50ml; Concentration of catalyst = 0.1M org. phase; Concentration of sulfide = 2.3M, MEA/H_2S ratio – 2.1; Stirring speed – 1500 rpm.

4.2.1.3 Effect of Catalyst (Amberlite IR 400) Quantity

The effect of catalyst (Amberlite IR 400) quantity on the conversion of benzyl chloride was studied in the concentration range of 0% (w/v) to 15% (w/v) of organic phase, as shown in Fig. 4.7. With the increase in catalyst quantity, the conversion of benzyl chloride as well as reaction rate increases.Only by increasing the catalyst concentration, benzyl chloride conversion of more than 90% was achieved whereas it was about 76% without catalyst even after 480 min of reaction under otherwise identical conditions. Fig. 4.7 also shows that over certain concentration of the catalyst, ca. 0.10 M of organic phase, the conversion of BC becomes constant. This could be attributed to interface saturation, which means that mass transfer of the active species into organic phase reaches a maximum value. The selectivity of DBS increases with increase in catalyst concentration as shown in Figure 4.8. Therefore, the selectivity of BM decreases with catalyst loading.

For liquid-liquid-solid tri-phase reactions, the overall rate of reaction is governed by rate of transportation of anions from aqueous phase to organic phase. In presence of PTC, the transportation of anions (in present case S^{2-} and HS^-) is facilitated and the reaction becomes organic-phase limited. The hydrosulfide (HS^-) and sulfide (S^{2-}) ions present in the aqueous phase readily form ion pairs [Q^+HS^- and $Q^+S^{2-}Q^+$], with quaternary cations, [Q^+], and are transferred to the organic phase and then reacts with benzyl chloride. With increased catalyst concentration, more amount of $[Q^+]_2S^{2-}$ ion pair is formed and transferred to the organic phase and reacts with benzyl chloride to form DBS. The selectivity of DBS, therefore, increases with increase in catalyst concentration.

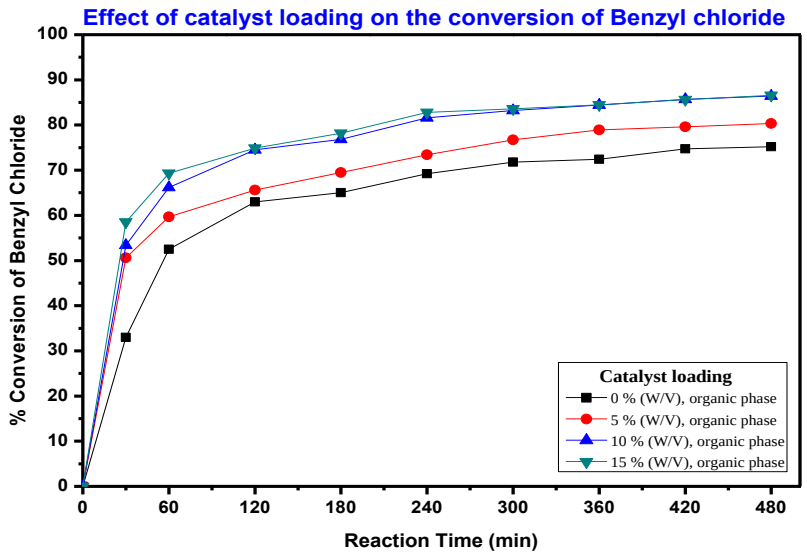


Fig. 4.7: Effect of the catalyst quantity on BC conversion

Operating Condition :Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M; Sulfide concentration – 2.3M; MEA/H_2S mole ratio – 2.1; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

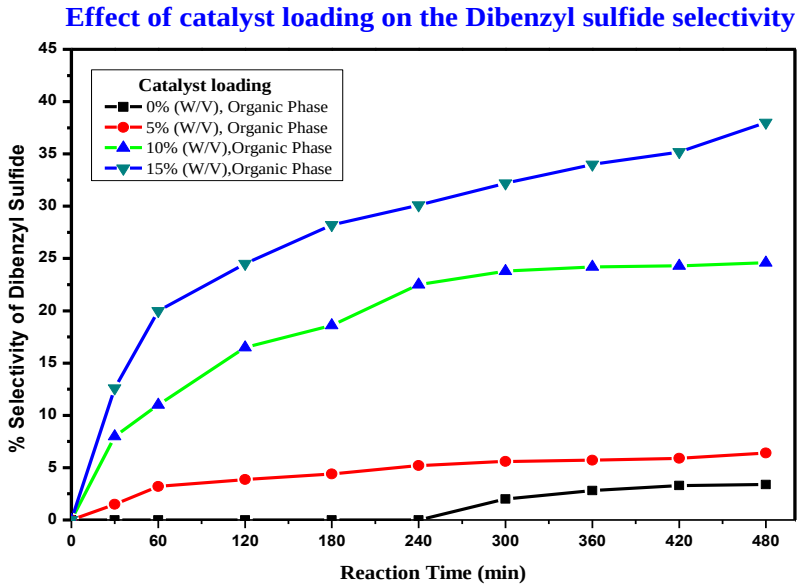


Fig. 4.8: Effect of the catalyst quantity on DBS selectivity

Operating Condition :Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M; Sulfide concentration – 2.3M; MEA/H_2S mole ratio – 2.1; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

4.2.1.4 Effect of Initial MEA: Sulfide Mole Ratio

The effect of initial MEA: Sulfide mole ratio on the conversion of benzyl chloride and the selectivity of various products were studied in two different ways: (1) by varying the initial concentration of sulfide keeping the initial concentration of MEA in the aqueous phase constant, and (2) by varying the initial concentration of MEA keeping the initial concentration of sulfide in the aqueous phase constant.

4.2.1.4.1 Effect of Initial Sulfideconcentration

The effect of MEA: sulfide mole ratio was studied by varying the initial sulfide concentration in the aqueous phase keeping MEA concentration fixed at 3.5M. For fixed MEA concentration, with an increase in MEA: sulfide ratio (or with a decrease in initial sulfide concentration in the aqueous phase), the conversion of BC decreases because of the limited quantity of sulfide in the aqueous phase as shown in Fig. 4.9. Keeping all other reaction conditions fixed, a conversion of more than 90% was achieved after 480 min of run.

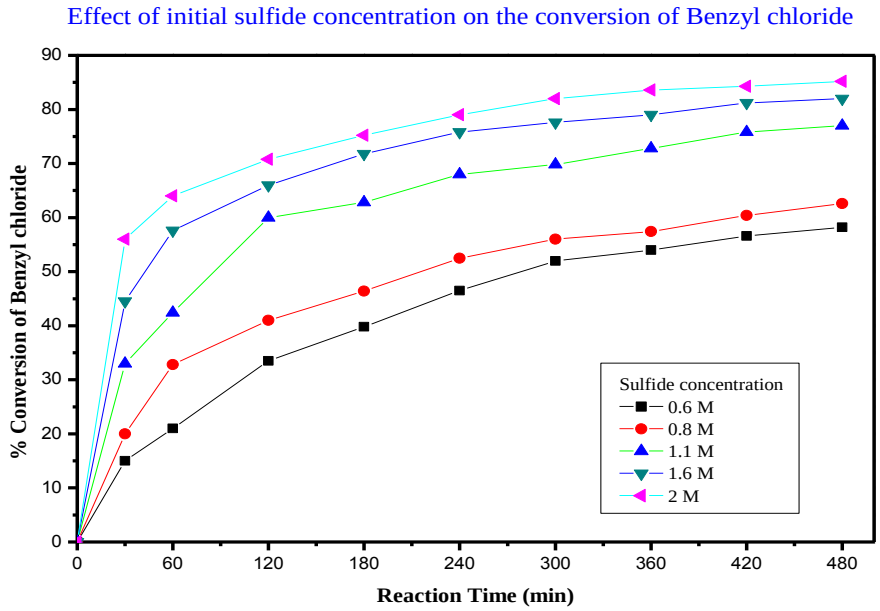


Fig. 4.9: Effect of initial sulfide concentration on BC conversion

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of MEA = 3.5 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

However, an opposite trend was observed for the selectivity of DBS. For a fixed conversion of benzyl chloride, the selectivity of DBS increases with an increase in MEA: sulfide mole ratio (or decrease in initial sulfide concentration) as shown in Fig. 4.10.Keeping all other reaction conditions fixed, a conversion of more than 78% was achieved after 480 min of run. However, an opposite trend was observed (Fig.4.10) for selectivity of DBS.Further increase of sulfide concentration results in decrease of selectivity of DBS as observed from the figure.

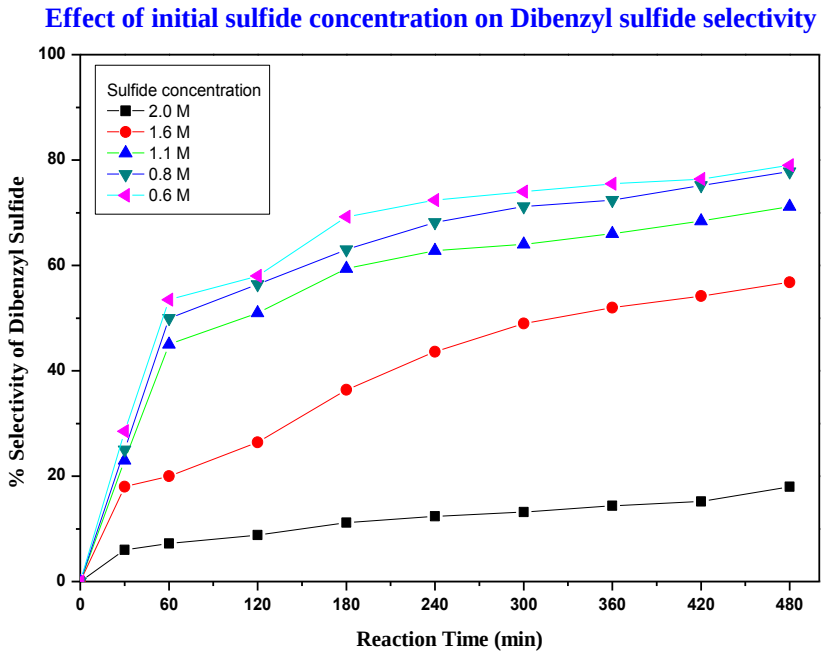


Fig. 4.10: Effect of initial sulfide concentration on DBS selectivity

Operating Condition:Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of MEA = 3.5 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

With increase in sulfide concentration, selectivity of DBS decreases. This can be explained by considering the fact that although MEA as such does not participate in the reaction with BC, it does affect the equilibrium among MEA, H_2S, and water, which results in two active anions, sulfide (S^{2-}) and hydrosulfide (HS^-), in the aqueous phase. These two active anions participate in two different reactions. In the presence of a base (MEA), the dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions, relative to hydrosulfide ions in the aqueous phase, increases as the MEA concentration increases.

Therefore, only by changing the MEA concentration with constant sulfide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.

4.2.1.4.2 Effect of initial MEA concentration

The concentration of MEA in the aqueous phase was varied maintaining a constant initial sulfide concentration of 1.86 M. To study the effect of MEAconcentration, the aqueous sulfide of different MEA concentrations (but having constant sulfide concentration) was prepared by taking 30 ml.of aqueous sulfide (with known sulfide and MEA concentrations,. then adding various proportions of pure MEA and distilled water to it in such a way that the total volume became 50 ml.in all the cases.With increase in MEA: Sulfide mole ratio (or with increase in MEA concentration in the aqueous phase), the conversion of benzyl chloride increases as shown in Fig. 4.11. For a fixed conversion of benzyl chloride, the selectivity of DBS increases with increase in MEA: sulfide mole ratio as shown in Fig. 4.12. Therefore, for a fixed conversion of benzyl chloride, the selectivity of BM decreases with an increase in MEA: sulfide mole ratio.

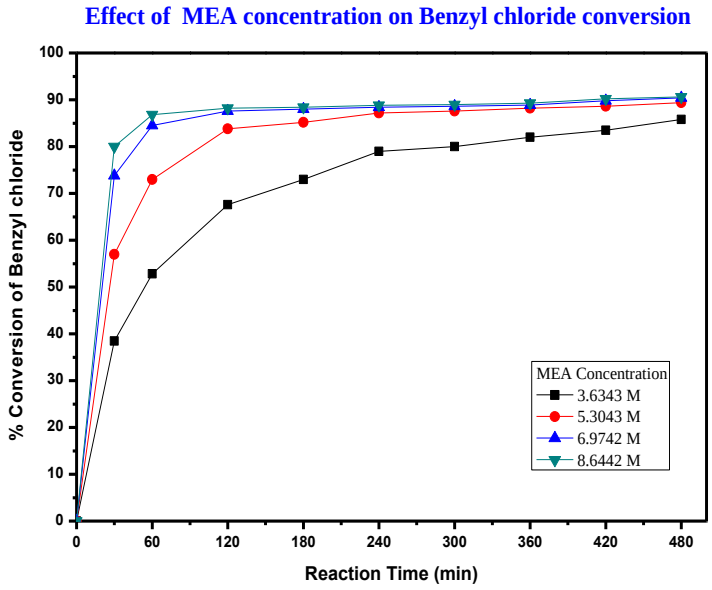


Fig. 4.11: Effect of MEA concentration on BC conversion

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of sulfide = 1.86 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

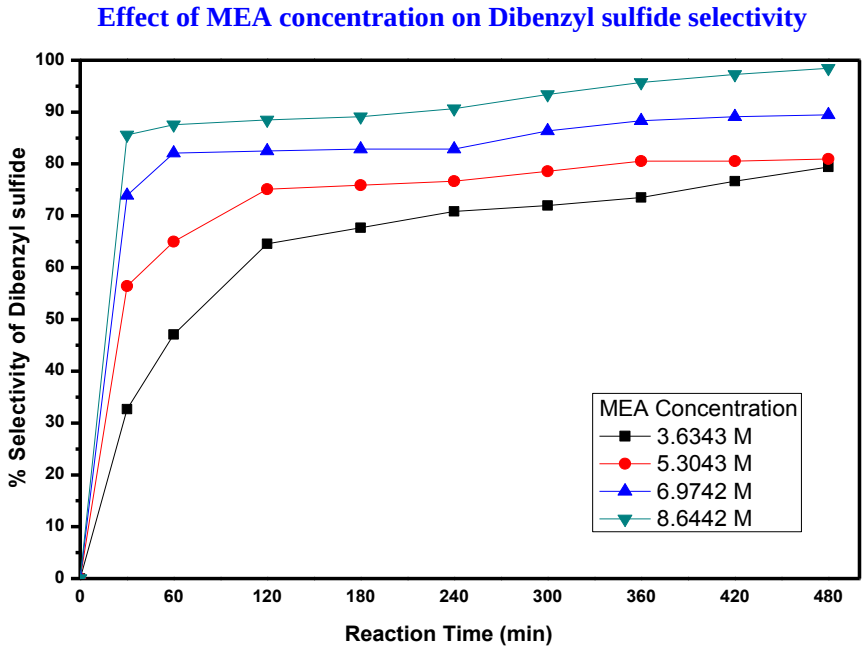


Fig. 4.12: Effect of MEA concentration on DBS selectivity

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of sulfide = 1.86 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

Although MEA does not take part in the reaction with benzyl chloride, it affects the equilibrium among MEA, hydrogen sulfide (H_2S), and water that results into two active anions, namely sulfide (S^{2-}) and hydrosulfide (HS^-), in the aqueous phase. The concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with an increase in MEA: sulfide mole ratio (due to increase in pH of the solution with increasing MEA concentration), which results in higher selectivity of DBS. As it is observed from the Scheme 4.1, one mole of sulfide reacts with two moles of benzyl chloride to form one mole of DBS whereas it requires only one mole of benzyl chloride to form one mole of BM. Although the initial concentration as well as the amount of sulfide in the aqueous phase remains the same, the conversion of benzyl chloride increases with an increase in MEA: sulfide mole ratio because of the higher selectivity of DBS at higher MEA: sulfide mole ratio. Therefore, only by changing the MEA concentration with constant sulfide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.

4.2.1.5 Effect of Concentration of Benzyl Chloride

The effect of benzyl chloride concentration on the conversion of benzyl chloride was studied at three different concentrations in the range of 1.75 – 4.25M as shown in the Fig. 4.13. It is seen from this figure that with an increase in the concentration of benzyl chloride, the conversion of benzyl chloride decreases because of limited quantity of sulfide present in the aqueous phase. With benzyl chloride concentration of 1.75M, almost 90% conversion of benzyl chloride was observed whereas the conversion of benzyl chloride was only about 62% with benzyl chloride concentration of 4.25M even after 480 min of reaction under otherwise identical experimental conditions as observed from the figure.

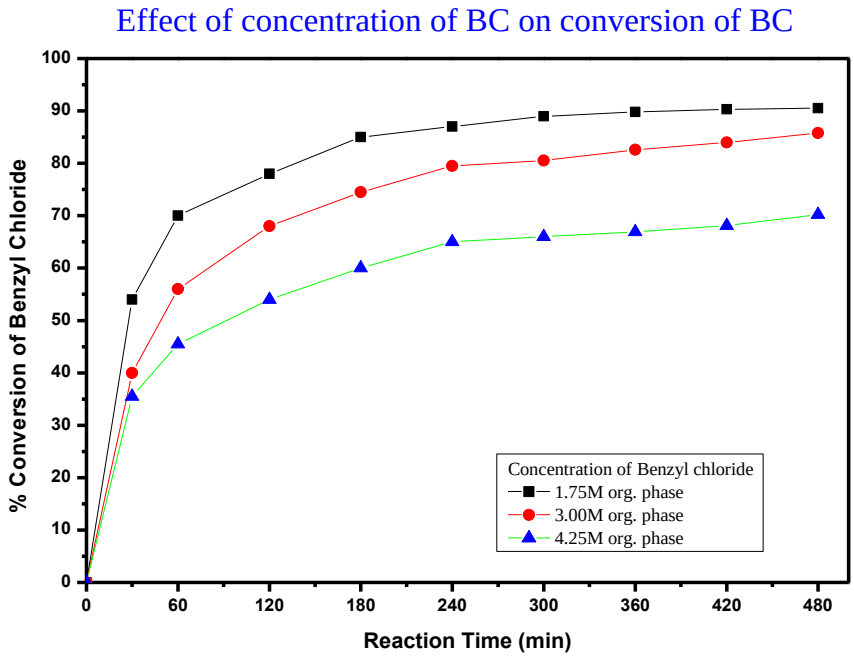


Fig. 4.13: Effect of concentration of BC on conversion of BC

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of sulfide = 1.86 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

The selectivity of DBS increases sharply with an increase in the concentration of benzyl chloride as shown in Fig. 4.14. As observed from the figure, the selectivity of DBS is about 55% for 4.25M of benzyl chloride concentration, whereas the selectivity of DBS is only about 16%

for 1.75M of benzyl chloride concentration even after 480 minutes of reaction under otherwise identical experimental conditions.

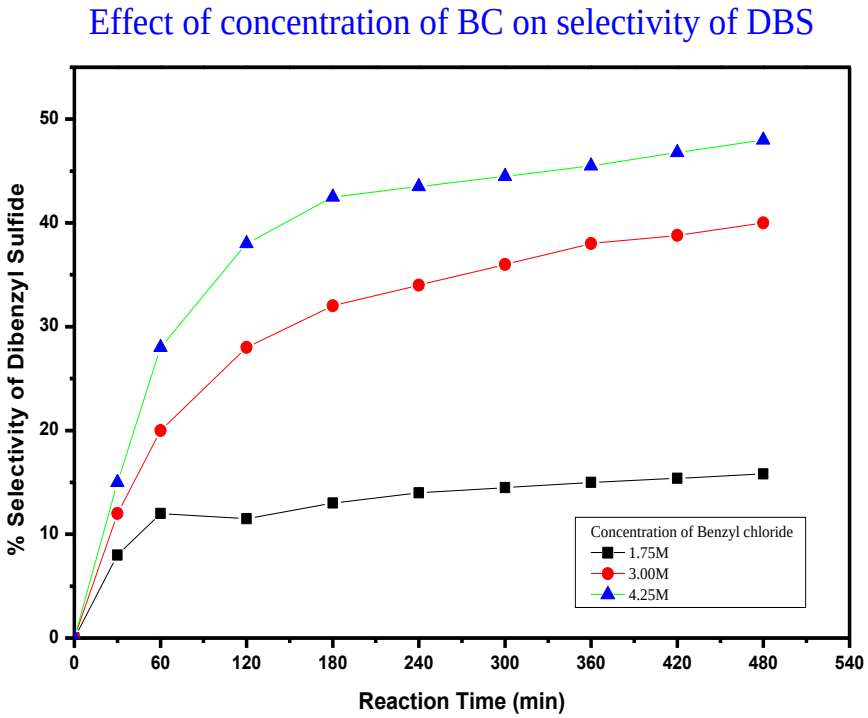


Fig. 4.14: Effect of concentration of BC on selectivity of DBS

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of benzyl chloride – 2.8M org. phase; Concentration of sulfide = 1.86 M;Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

From the plot of selectivity of DBS vs conversion of BC (Fig. 4.15), it is seen that there is a sharp increase of slope of the curve with increase in the concentration of BC. It is also observed from the figure that the selectivity of BM is higher than that of DBS during the initial stage of the reaction. Therefore, it can be concluded that the reaction leading to the formation of BM is very fast as compared to that leading to the formation of DBS. Therefore, at lower benzyl chloride concentrations, there will be insufficient quantity of benzyl chloride present to produce DBS, which results in low selectivity of DBS.

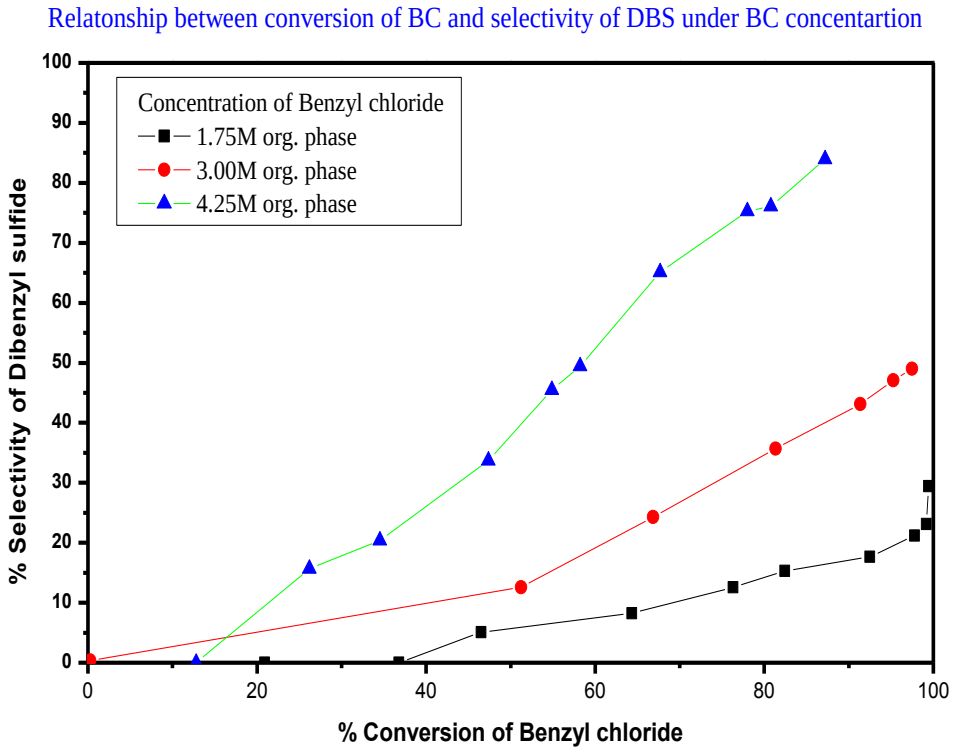


Fig. 4.15: Relationship between conversion of BC and selectivity of DBS under different BC concentrations

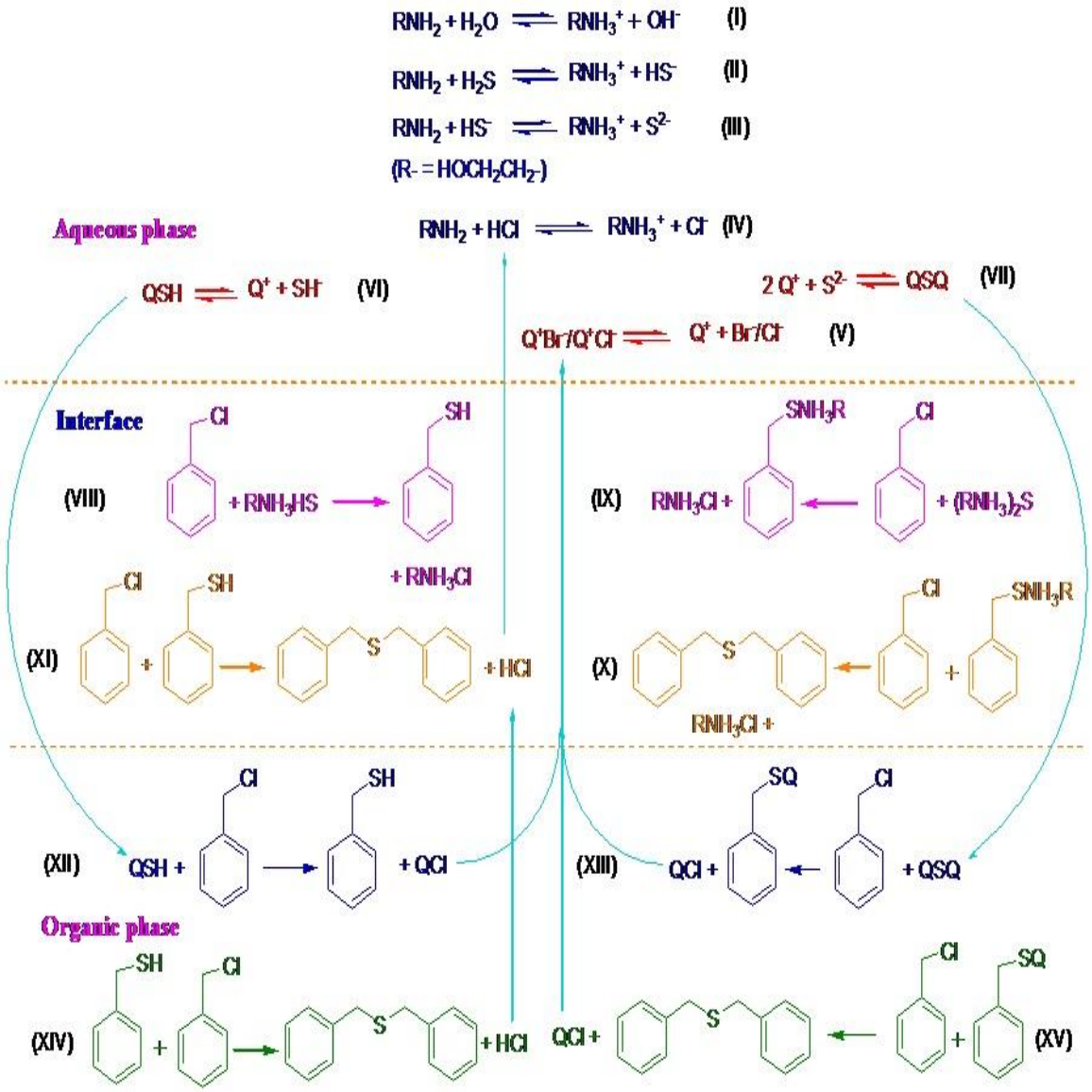
Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of sulfide = 1.86 M;Concentration of MEA = 3.5 M; Concentration of catalyst = 0.1M org. phase; Temperature – 45^0C; Stirring speed – 1500 rpm.

With lower benzyl chloride concentrations in the organic phase, almost complete conversion of benzyl chloride was achieved. This resulted in very low selectivity of DBS, that is, high selectivity of BM and incomplete sulfide utilization in the aqueous phase. On the other hand, with an excess of benzyl chloride, higher DBS selectivity was achieved with efficient utilization of sulfide in the aqueous phase although the benzyl chloride conversion remained low. Therefore, a question of optimization among the opposing factors (conversion of benzyl chloride, utilization of sulfide**,** and selectivity of DBS) arises, and needs to be addressed.

4.2.2Mechanistic Investigation

The reaction of benzyl chloride with H_2S-rich aqueous MEA was studied in the presence of tri-phase transfer catalyst Amberlite IR 400, which is not so lipophilic one and, therefore, the reaction can be represented by extraction mechanism as shown by scheme 4.2. Generally, the reactions in the aqueous phase are fast compared to the reactions in the organic phase. Therefore, there exists an ionic equilibrium among MEA, H_2S, and water, which results three active anions: hydroxide (OH^-), hydrosulfide (HS^-), and sulfide (S^{2-}) as represented by the Eqs. (I)- (III) in Scheme 4.2. These ions are capable of producing ion pairs (QOH, QSH, and QSQ) with quaternary ammonium cation, Q^+ [$(C_4H_9)_4N^+$]. However, no benzyl alcohol, $C_6H_5CH_2OH$ or benzyl amine $C_6H_5CH_2NH_2$ (substitution product of QOH), was identified in the GLC analysis of the two-phase reaction products in the presence of Amberlite IR 400. This is because of the fact that the active catalyst, QOH, is more hydrophilic in nature and not easily transferred to the organic phase (Wang and Tseng, 2003), and therefore, the hydrolysis of benzyl chloride under weak alkaline medium of aqueous ammonium hydroxide is slow (Yadav et al., 2003a). However, only two species (QSH and QSQ) are generated and transferred to the organic phase where the reaction takes place.

In some of the research articles, it was reported that the sulfide ions present in the aqueous phase are first converted to the hydrosulfide ($S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$), which in turn is transferred to the organic phase and reacts with benzyl chloride to produce DBS via phase transfer catalysis. This is supported by the fact that the selectivity of DBS increases with an increase in MEA: sulfide mole ratio as discussed previously (Yadav 2003a). Therefore, it can be concluded that the active catalysts ($Q^+S^{2-}Q^+$ and Q^+SH^-) formed from the sulfide ions and hydrosulfide ions present in the aqueous phase are transferred to the organic phase and react with benzyl chloride to produce DBS and BM, respectively.



Scheme 4.2: Mechanism of Liquid-Liquid-Solid phase transfer Catalyzed reaction of BC with H_2S-rich aqueous-monoethanolamine in presence of Amberlite IR 400 (Tri-phase catalyst)

Fig. 4.16 shows the concentration profile for a typical batch. It is seen from the figure that concentration of BM reaches a maximum and then falls gradually with time. Therefore, BM is converted to the DBS whose concentration increases with time. Probably, benzyl chloride reacts with BM to produce DBS and hydrochloric acid. Since, the hydrochloric acid (strong acid) is formed from a weak acid, BM, this reaction is expected to be slow and is favored only by the

presence of ammonium hydroxide, which reacts with hydrochloric acid irreversibly to produce ammonium chloride in the aqueous phase.

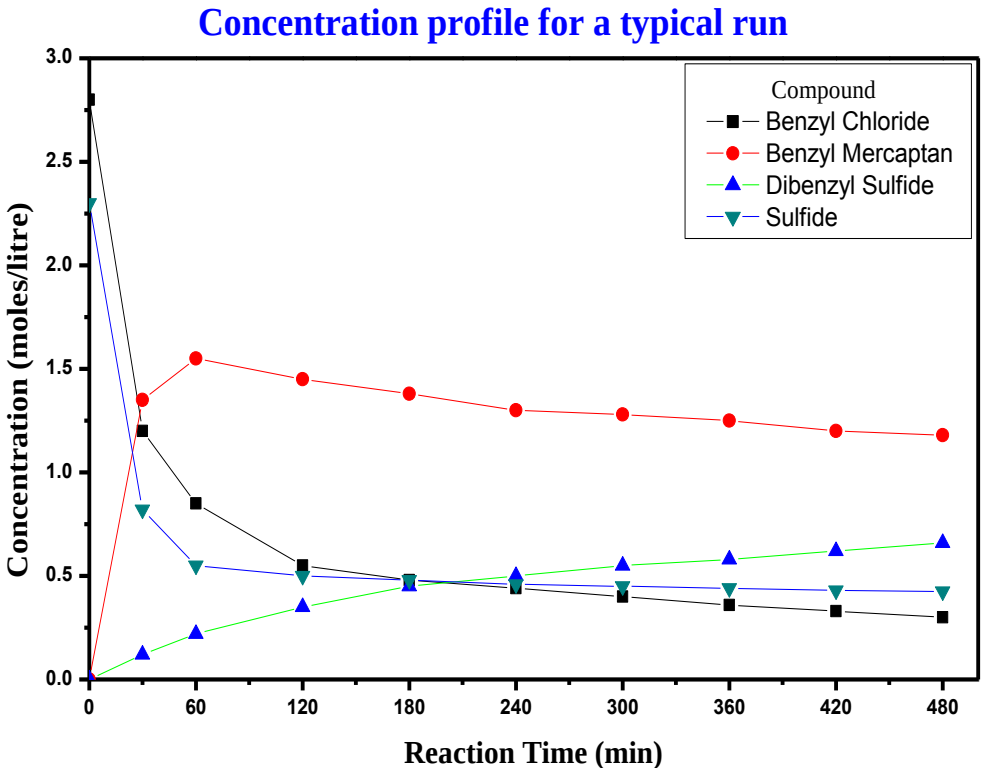


Fig. 4.16: Concentration profile for a typical run

Operating Condition: Volume of organic phase – 50ml; Volume of Aqueous Phase – 50ml; Concentration of BC = 2.8 M; Concentration of sulfide = 1.86 M; Concentration of MEA = 3.5 M; Concentration of catalyst = 0.1M org. phase; Temperature – 45 ^{0}C; Stirring speed – 1500 rpm.

Two mechanisms, interfacial and extraction, are generally used to explain the liquid-liquid phase transfer catalysis, based on the lipophilicity of the quaternary cation. The extraction mechanism, suggested by Starks (1971) and Starks and Liotta (1978), is applicable to those catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phase. In the interfacial mechanism, catalyst remains entirely in the organic phase because of its high lipophilicity and exchanges anions across the liquid-liquid interface (Dehmlow and Dehmlow, 1983).

Ethanolammonium sulfide ($(HOCH_2CH_2NH_3)_2S$) and hydrosulfide ($HOCH_2CH_2NH_3SH$) are formed in the aqueous phase. In non-catalyzed reaction, these two species are expected to react with BC at the aqueous-organic interface (as they are insoluble in organic phase). Based on the product distribution, the mechanism of the non-catalytic reactions was represented by the reactions VIII-XI of Scheme 4.2. The Ethanolammonium hydrosulfide and sulfide in the aqueous phase non-catalytically react with organic phase benzyl chloride ($C_6H_5CH_2Cl$) at the interface to yield benzyl mercaptan ($C_6H_5CH_2SH$) and Dibenzyl sulfide ($(C_6H_5CH_2)_2S$), respectively. The nucleophilic substitution reactions are in general 2^{nd} order overall. The direct reaction of BC with $(RNH_3)_2S$ (R= $HOCH_2CH_2$) was therefore assumed to proceed through an intermediate, $C_6H_5CH_2NH_3R$, which further reacts with $C_6H_5CH_2Cl$ to produce $(C_6H_5CH_2)_2S$. The $C_6H_5CH_2SH$reacts further with $C_6H_5CH_2Cl$ to produce $(C_6H_5CH_2)_2S$ (reaction XI of Scheme 4.2). This conclusion was reached from the concentration profile of a typical batch (Fig. 4.14).

The reaction in presence of catalyst is expected to proceed through both catalytic and non-catalytic pathway as shown in the Scheme 4.2. In the catalytic pathway, phase transfer cation Q^+ exchanges ion with ethanolammonium sulfide ($(HOCH_2CH_2NH_3)_2S$) and hydrosulfide ($HOCH_2CH_2NH_3SH$) to form ion-pairs $Q^+S^{2-}Q^+$ and Q^+SH^- which, being organophilic in nature, transfer to the organic phase and reactants with BC to form BM and DBS (reactions XII — XV in Scheme 4.2).

4.3 Recycle and Reusability of Catalyst (Amberlite IR 400)

After the completion of the kinetic run, the agitation was stopped and the phases were allowed to separate into three layers (L-L-S). When the phases were clearly separated, the organic phase containing the product was removed. The reusability was found to be good up to four uses and there was a loss in conversion during the fifth time since the amount of third phase was less in comparison with the previous runs as shown in Fig.4.17.

After use the catalyst microsphere was filtered from the solution by the use of filter paper. It was washed with acetone and water and was dried to remove the adsorbed substance. The catalyst obtained was reused and the data obtained is shown in below figure.

Fig. 4.17 shows the conversion of benzyl chloride with the cycle number. It can be seen that after 4 cycles, the activity of tri phase catalyst Amberlite remains nearly unchanged. This tells that Amberlite has got excellent reuse property and high stability.

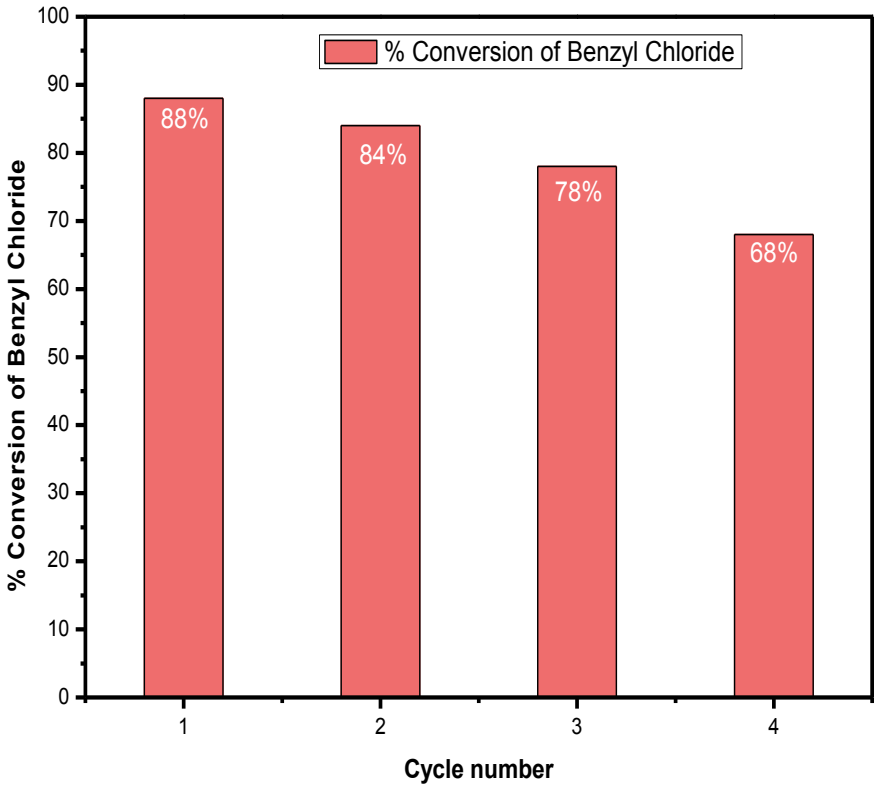


Fig.4.17: Effect of cycle number of reuse on the catalytic activity.

Operating condition: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of benzyl chloride – 2.8M, Sulfide concentration – 2.3M, MEA/H_2S ratio–2.1, Temperature – 45 ^{0}C, catalyst loading = 10%(w/v), Stirring speed – 1500 rpm.

CHAPTER 5

SUMMARY AND CONCLUSIONS

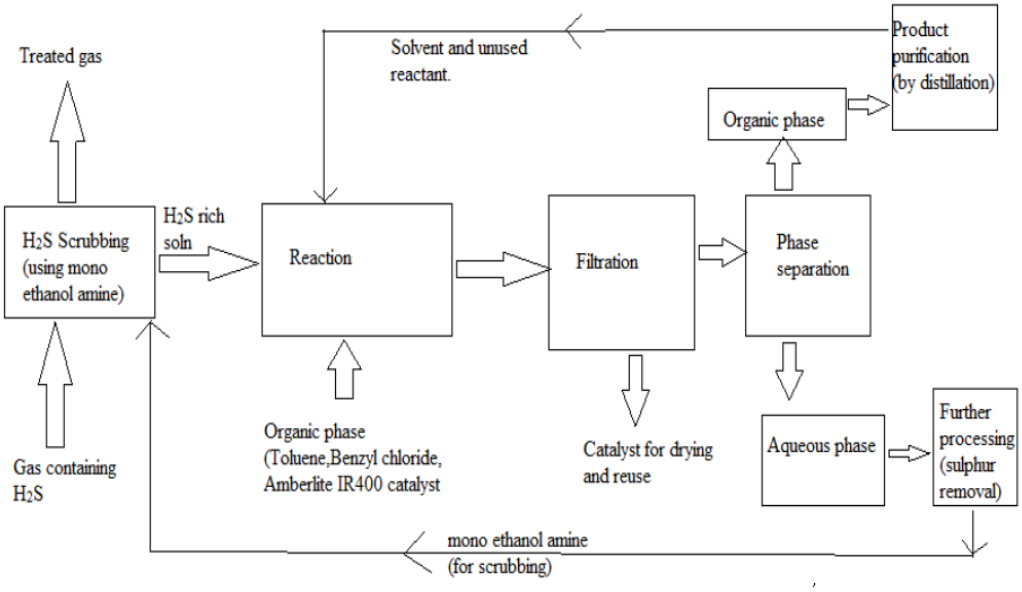
Chapter 5

Summary and Conclusions

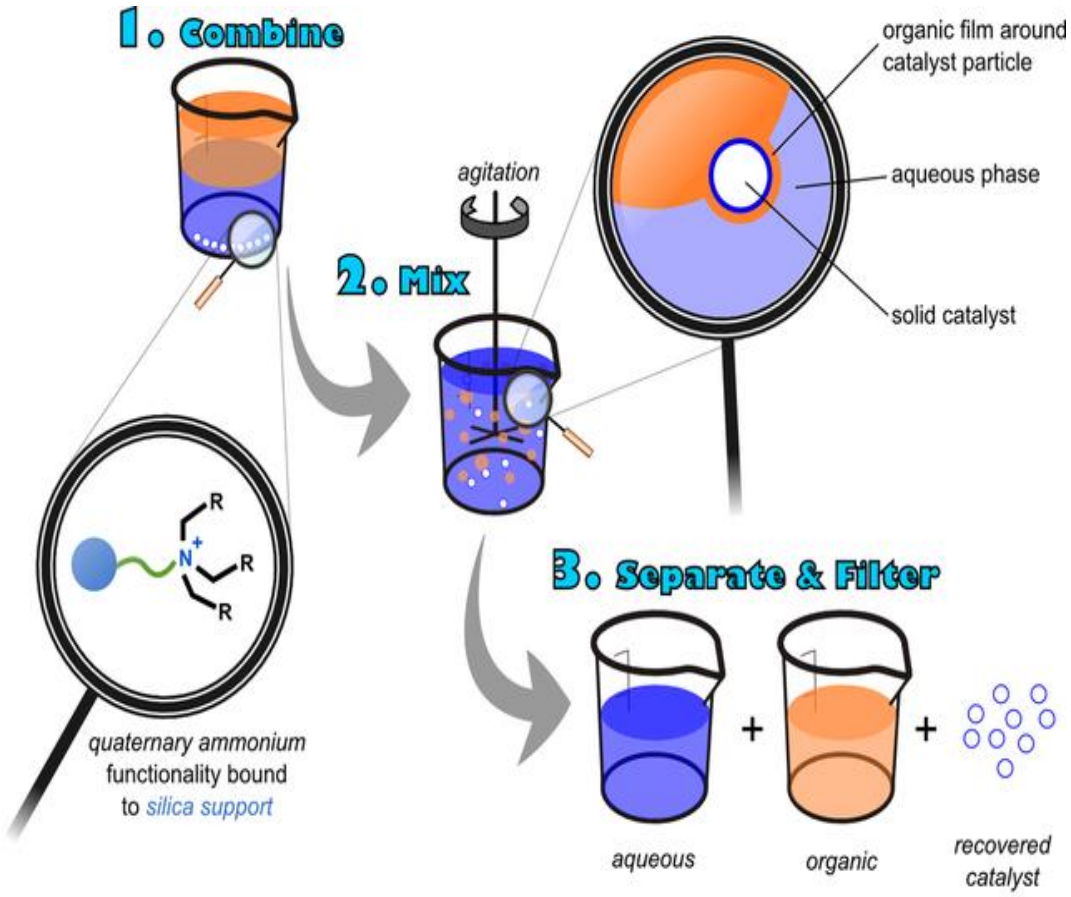
Abstract

This chapter summarizes the concluding remarks from the preceding chapter.

The present work carried out in this thesis leadsto the development of a state-of-the-art process to produce value-added chemicals utilizing the H_2S present in various byproduct gas streams. In accordance with the present process, the H_2S present in the gas streams can be utilized to produce value-added products in two steps: (1) removal of H_2S from gas stream by conventional methods (alkanolamine-based processes), followed by (2) production of value-added chemicals utilizing H_2S-rich solution obtained from the first step of the process. Since the removal of H_2S by alkanolamines are well established and industrially practiced one, the present work deals with a detailed study on the production of value-added chemicals utilizing H_2S-rich aqueous alkanolamine in the batch mode. The ammonia-based process is suitable for the gas streams containing both NH_3 and H_2S because both the impurities can be removed simultaneously in a single step, where as alkanolamines-based process can be used for gas streams containing no ammonia because of its other advantages over the ammonia. The strategy of the present process is schematically represented by Scheme 5.1, 5.2.



Scheme 5.1 Schematic representation of strategy of present process



Scheme 5.2 Schematic representation of strategy of present process

The value-added chemicals produced in the present study are dibenzyl sulfide (DBS) and benzyl mercaptan (BM) from benzyl chloride (BC). The reaction of benzyl chloride with H_2S-rich aqueous alkanolamines was conducted batch-wise in presence (Chapter 4) in presence of an organic solvent (toluene) under Liquid-Liquid-Solid mode with a phase transfer catalyst (PTC), Amberlite IR 400. The influence of various process variables (stirring speed, catalyst loading, concentration of reactant, and temperature, alkanolamines concentration, elemental sulfur loading) on the reaction rate, conversion, and selectivity was studied. A suitable mechanism was established utilizing the effects of various parameters on the reaction rate and conversion to explain the course of the reaction.

The reaction of benzyl chloride with H_2S-rich aqueous MEA is of great industrial relevance, which could lead to different products (DBS and BM) of commercial value. This reaction was investigated in detail under liquid-liquid phase transfer catalysis conditions. One can selectively prepare either DBS or BM using the same reagents only by selecting

appropriate experimental conditions. A high MEA: sulfide mole ratio, high benzyl chloride concentration, low ammonium sulfide volume, and long reaction time lead to the selective preparation of DBS. On the other hand, opposite trend was observed for BM. With higher benzyl chloride concentration and lower ammonium sulfide volume, the conversion of benzyl chloride remains low with efficient sulfide utilization in the aqueous phase, whereas with lower benzyl chloride concentration and higher ammonium sulfide volume, almost complete conversion of benzyl chloride was observed although the utilization of sulfide in the aqueous phase remains low.

The reaction is kinetically controlled with an apparent activation energy value of 40.7 KJ mol^{-1}. A change in temperature and catalyst concentration changes only the reaction rate without significantly affecting the selectivity. The process involves a complex mechanism. The existence of an ionic equilibrium among MEA, H_2S, and water, producing sulfide and hydrosulfide ions in the aqueous phase was established. The two active ion pairs ($Q^+S^{-2}Q^+$ and Q^+SH^-) formed in the aqueous phase are first transferred to the organic phase and then react with benzyl chloride to produce DBS and BM, respectively. DBS is also formed by the reaction of BM and benzyl chloride.

The developed lab-scale process will be helpful in setting up indigenous manufacturing facilities for organic sulfides, mercaptans and anilines. The present process could be considered as an alternative to conventional processes (Claus or LO-CAT) because it is possible to produce commercially important chemicals in a cost-effective way. The work is also relevant to the global problem of pollution control caused by H_2S, SO_2 etc. and waste minimization.

In the reaction of benzyl chloride with H_2S-rich aqueous MEA, almost complete sulfide utilization in the aqueous phase was observed under certain experimental conditions. Therefore it needs no further treatment (tail gas treatment unit as in the Claus process) before its reuse for the removal of H_2S. Therefore, present process has enormous potential to be considered as a viable alternative to conventional process (Claus or LO-CAT).

CHAPTER 6

SCOPE FOR FURTHER WORK

Chapter 6

Scope for Further Work

Abstract

This chapter recommends the possibility for future work based on the observations, results and conclusions drawn from the present study. This chapter has been planned to identify the areas where improvement can be done on the same systems to get better conversion and selectivity and to get rid of some problems faced here. Also, how the present procedure can be used to explore more in the field of phase transfer catalysis has been discussed.

6.1 Investigation of Mechanistic Pathways

As can be seen from chapter4, the mechanistic pathways shown for the reaction ofbenzyl chloride with H_2S-rich alkanolamine (Scheme 4.2) are based partly on some earlier studies and partly from the data of the present studies. Aqueous phase can be analyzed to know the presence of several species (Cl^-, Br^-, HS^-, S^{2-}, Q^+ etc.) in it and then to quantify it to get better insight into the mechanistic pathway in the aqueous phase of the triphasic reaction system. This study will help to establish the reaction mechanism accurately, and then to perform kinetic modelling.

6.2 Finding out Effect of other Parameters

The effect of pH of H_2S-rich alkanolamine solution needs to beexplored. S^{2-}/HS^- ratio plays an important role in selectivity of benzyl mercaptan and benzyl sulfide (Schemes 4.2), which in turn depends on the pH of the alkalinesolution. Effects of other anions as co-catalyst and addition of alkali that can influence the reaction rate and selectivity of desired products can also be tried.

6.3 Use of Other Aqueous Phase

The aqueous phase used in the present work is monoethanolamine which can absorb both CO_2 and H_2S. Our present work is applicable for the stream containing H_2S and CO_2, only if the aqueous phase is H_2S selective.

6.4 Exploring the Possibilities of other Value-added Products

Some other industrially important sulfides or mercaptans can be synthesizedselectively by using H_2S-rich amines. H_2S can also be converted to soluble disulfide (S_2^{2-}) or bisulfide (HS^-)preferentially to produce organic disulfide (dibenzyldisulfide) or thiols selectively.

6.5 Large-scale Application of the Present Process

The present systems need to be tried out in a scaled-up set-up to check out the performance of the presence process before applying for large-scale utilization. In ourpresent study, separation and purification of the products have not been tried out. It canbe tried out after carrying out reaction in bigger scale, separating the phases by separatingfunnel, separating the organic liquid component by either distillation or other chemicalmethods depending on the nature of components. Also identification of the products canbe done by using different available techniques like NMR, FTIR or MS. Simultaneousidentification and quantification can also be done in GC-MS.

REFERENCES

References

Akhnazarova, S.; Kafarov, V. Experiment Optimization in Chemistry and ChemicalEngineering.Mir Publishers, Moscow, **1982**.

Al-Baghli, N. A.; Pruess, S. A.; Yesavage, V. F.; Selim, M. S.A Rate-based Model forthe Design of Gas Absorbers for the Removal of CO_2 and H_2S Using AqueousSolutions of MEA and DEA.*Fluid Phase Equilibria***2001**, *185*, 31-43.

Asai, S.; Tajiri, H.; Hikita, H. Simultaneous Absorption of Hydrogen Sulfide andAmmonia into Water.*Gas Separation & Purification* **1989**, *3*, 7-12.

Austgen, D. M.; Rochelle, G. T.; Peng, X.; Chen, C. Model of Vapor-Liquid Equilibriafor Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTLEquation.*Industrial & Engineering Chemistry Research* **1989**, *28*, 1060-1073.

Bally, A. P. Erdol und Kohle, Vol. 14, pp. 921-923, **1961.**

Bandgar, B. P.; Sadavarte, V. S.; Pawar, Suchita G.; Kamble, V. T. Clean and EfficientSynthesis of Thioethers under Mild and Nonaqueous Conditions. *Indian Journalof Heterocyclic Chemistry* **2000**, *10(2)*, 159-160.

Beutier, D.; Renon, H. Representation of NH_3-H_2S-H_2O, NH_3-CO_2-H_2O, and NH_3-SO_2-H_2O Vapor-Liquid Equilibria.*Industrial & Engineering Chemistry ProcessDesign and Development* **1978**, *17(3)*, 220-230.

Bhave, R. R.; Sharma, M. M. Kinetics of Two-Phase Reduction of Aromatic NitroCompounds by Aqueous Solutions of Sodium Sulfides.*Journal of ChemicalTechnology and Biotechnology* **1981**, *31*, 93-102.

Bittell, J. E.; Speier, J. L. Synthesis of Thiols and Polysulfides from Alkyl Halides,Hydrogen Sulfide, Ammonia, and Sulfur.*Journal of Organic Chemistry* **1978**,*43(9)*, 1687-1689.

Blohm, C. L., and Riesenfeld, F. C.: **1955**, US. Patent 2,712,978.

Bottoms, R. R., **1930**, U.S. Patent 1,783,901; Re **1933**, 18,958.

Box, G.E.P.; Hunter, W. G.; Hunter, J.S. Statistics for Experimenters.John Wiley andSons, New York, **1978**.

Box, G.E.P.; Wilson, K.B.On the experimental attainment of optimum conditions.J.Roy. Stat. Soc. Ser. B. Method. 13 (**1951**) 1–45.

Bromley, L.A. Thermodynamic properties of strong electrolytes in aqueous solutions*AIChE Journal* **1973**, *19 (2)*, 313–320.

Choi, J.; Yoon, N. M. Synthesis of Thiols via Palladium CatalyzedMethanolysis ofThioacetateswithBorohydride Exchange Resin. *Synthetic Communications***1995a**, *25(17)*, 2655-2663.

Choi, J.; Yoon, N. M. Direct Synthesis of Thiols from Halides and Epoxides usingHydrosulfide Exchange Resin in Methanol.*Synthesis* **1995b**, *4*, 373-375.

Cline, E. L.; Reid, E. E.Some Derivatives of Ethylbenzene.*Journal of AmericanChemical Society* **1927**, *49*, 3150-3156.

Dauben, W. G. Organic Reactions, John Wiley & Sons, Inc.: New York, **1973,** Vol. 20,p455.

Dehmlow, E. V.; Dehmlow, S. S. Phase Transfer Catalysis, 2nd ed., VerlagChemieWeinheim, **1983**.

Edwards, T.J., Newman, J., Prausnitz, J.M., 1975. Thermodynamics of aqueous solutionscontaining volatile weak electrolytes.*AIChE Journal* **1975**, *21 (2*), 248–259.

Frazier, H. D. and Kohl, A. L. "Selective Absorption of H_2S from Gas Streams," **Ind.Eng. Chem.** Vol. 42, **1950**, pp. 2282-2292.

Gilman, H. Organic Syntheses. Collective volume 1, John Wiley & Sons, Inc.: NewYork, **1941**, p-52.

Hamblin, R. Removal and Recovery of Sulfur from a Gas Stream Containing HydrogenSulfide. Patent No. US3728441, **1973**.

Han, X.; Zhou, R.; Lai, G.; Yue, B.; Zheng, X. Effect of Transition Metal (Cr, Mn, Fe,Co, Ni and Cu) on the Hydrogenation Properties of Chloronitrobenzene OverPt/TiO2 Catalysts. *Journal of Molecular Catalysis A: Chemical* **2004**, *209*, 83-87.

Harvey, W. W.; Makrides, A.C. Process for Removing Hydrogen Sulfide and Ammoniafrom Gaseous Streams.Patent No. US4192854, **1980**.

Heather, J.B. Method for Preparation of Benzyl Mercaptan. *U.S. patent No. 4740623*,**1988**.

Hoffman, W. S.*;* Reid, E. E. Derivatives of Anthraquinone.Reactions of AnthraquinoneSulfonic Acids with Mercaptans.*Journal of American Chemical Society* **1923**, 45,1831-1838.

Hojo, M.; Takagi, Y.; Ogata, Y. Kinetics of the Reduction of Nitrobenzene by SodiumDisulfide. *Journal of the American Chemical Society* **1960**, *82*, 2459-2462.

Ido, T.; Susaki, T.; Jin, G.; Goto, S. Characteristics of Third Phase for Reaction of BenzylChloride with Sodium Sulfide in Phase Transfer Catalytic System. *AppliedCatalysis A: General* **2000**, *201*, 139–143.

Idoux, J. P.; Plain, W. Selective Reduction of Dinitrobenzenes.An Organic LaboratoryExperiment.*Journal of Chemical Education* **1972**, *49(2*), 133.

Iranpoor, N.; Firouzabadi, H.; Shaterian, H. R. A New Approach to the Reduction ofSulfoxides to Sulfides with 1,3-Dithiane in the Presence of Electrophilic Bromineas Catalyst. *Journal of Organic Chemistry* **2002**, *67(9)*, 2826-2830.

Isaacs, E. E.; Otto, F. D.; Mather, A. E. Solubility of Mixtures of H_2S and CO_2 in aMonoethanolamine Solution at Low Partial Pressures. *Journal of ChemicalEngineering Data* **1980**, *25*, 118-120.

Islam, M.A.; Sakkas,V.; Albanis,T.A. Application of statistical design of experimentwith desirability function for removal of organophosphorus pesticide fromaqueous solution by low-cost material, *J. Hazard. Mater.***2009**, *170*, 230-238.

Jwo, J.J. Phase Transfer Catalysis: Fundamentals and Selected Systems, *Catalysis Reviews: Science and Engineering* **2003**, vol. 45, Issue 3-4.

Kaewsichan, L.; Al-Bofersen, O.; Yesavage, V. F.; Selim, M. S. Predictions of thesolubility of acid gases in monoethanolamine (MEA) and methyldiethanolamine(MDEA) solutions using the electrolyte-UNIQUAC model. *Fluid PhaseEquilibria***2001**, *183–184*, 159-171.

Kirk-OthmerEncyclopedia of Chemical Technology, John Wiley and Sons, New York,Vol-22, P-267-289, **1983**.

Kohl, A. L. "Selective H_2S Absorption-A Review of Available PTO Processes," Petrol.

Kohl, A.L.; Nielsen, R.B. Gas purification, Gulf Publishing Company Houston, Texas,**1997**.

Labat, Y. Synthesis of Benzyl Mercaptan. *European Patent No.EP0337838*, **1989**.

Lakouraj, M. M.; Movassagh, B.; Fadaei, Z. Synthesis of Organic Sulfides via the$Zn/Alcl_3$ System in Aqueous Media.*Synthetic Communications* **2002**, *32(8)*,1237-1242.

Lauwiner, M.; Rys, P.; Wissmann, J. Reduction of Aromatic Nitro Compounds withHydrazine Hydrate in the Presence of an Iron Oxide Hydroxide Catalyst. I. TheReduction of MonosubstitutedNitrobenzenes with Hydrazine Hydrate in the

Presence of Ferrihydrite.*Applied Catalysis A: General* **1998**, *172*, 141-148.

Lawson, J. D.; Garst, A. W. Gas Sweetening Data: Equilibrium Solubility of HydrogenSulfide and Carbon Dioxide in Aqueous Monoethanolamine and AqueousDiethanolamine Solutions. *Journal of Chemical Engineering Data* **1976**, *21(1)*,20-30.

Lee, J. II; Otto, F. D.; Mather, A. E. Equilibrium in Hydrogen Sulfide-Monoethanolamine-Water System.*Journal of Chemical Engineering Data* **1976**,*21(2)*, 207-208.

Lele, S.S., Bhave, R.R., Sharma, M.M. Fast and very low liquid–liquid reaction: phasetransfer catalysis. *Chemical Engineering Science* **1983**, *22*, 765–773.

Maity, S.K.; Pradhan N.C; Patwardhan, A. V. Reaction of benzyl chloride withammonium sulfide under liquid–liquid phase transfer catalysis: Reactionmechanism and kinetics, *Appl. Catal. A: Gen*. **2006a**, *250*, 114–121.

Maity, S.K.; Pradhan N.C; Patwardhan, A. V. Kinetics of the reduction of nitrotoluenesby aqueous ammonium sulfide under liquid–liquid phase transfer catalysis, *Appl.Catal. A: Gen.* **2006b**, *301*, 251–258.

Maity, S.K.; Pradhan N.C; Patwardhan. Kinetics of Reduction of Nitrotoluenes by H_2SRichAqueous Ethanolamine, *Ind. Eng. Chem. Res.* **2006c,** *45*, 7767-7774.

Maity, S.K.; Pradhan N.C; Patwardhan. Reduction of *o*-nitroanisole to *o*-anisidinebyH$_2$S-rich aqueous diethanolamine:Anovel process for utilization ofH2S-ladengas streams, *Chem. Eng. Sc.* **2007**, *62*, 805-813.

Manning, F. S., and Thompson, R. E. Oirfield Processing of Petroleum, Vol. one:Natural Gas, Pennwell Publishing Co., Tulsa, OK**, 1991**.

Melville, J. B.; Goddard, J. D.A Solid-Liquid Phase-Transfer Catalysis in Rotating-DiskFlow. *Industrial & Engineering Chemistry Research* **1988**, *27*, 551-555.

Meindl, W. R.; Angerer, E. V.; Schonenberger, H.; Ruckdeschel, G. Benzylamines:Synthesis and Evaluation of Antimycobacterial Properties. *Journal of MedicinalChemistry* **1984**, *27*, 1111-1118.

Meissner. R. E., 1983. "A Low Energy Process for Purifying Natural Gas," Proceedingsof the 1983 Gas Conditioning Coilfereizce, University of Oklahoma, Norman,OK.

Meissner, R. E. and Wagner, U., 1983, Oil and Gas J., Feb. 7, pp. 55-58.

Miller, S. J.; Collier, T. R.; Wu, W. Efficient Reduction of Sulfoxides with 2,6-Dihydroxypyridine. *Tetrahedron Letters* **2000**, *41(20)*, 3781-3783.

Miller, F. E., and Kohl, A. L., "Selective Absorption of Hydrogen Sulfide,''Oil and GaJ., Vol. 51, April 27, pp. 175-183, **1953**.

Mohammadpoor-Baltork, I.; Memarian, H. R.; Bahrami, K. 3-CarboxypyridiniumChlorochromate-Aluminium Chloride-An efficient and Inexpensive ReagentSystem for the Selective Oxidation of Sulfides to Sulfoxides and Sulfones inSolution and Under Microwave Irradiation. *Canadian Journal of Chemistry* **2005**,*83*, 115-121.

Montgomery, D.C. Design and Analysis of Experiments, fifth ed., John Wiley and Sons,New York, USA, **2001**.

Movassagh, B.; Mossadegh, A. Reductive Cleavage of S-S Bond by Zn/$AlCl_3$ System: ANovel Method for the Synthesis of Sulfides from Alkyl Tosylates and Disulfides.*Synthetic Communications* **2004a**, *34(13)*, 2337-2343.

Movassagh, B.; Mossadegh, A. Reductive Cleavage of S-S Bond by Zn/$Alcl_3$ System.ANovel Method for the Synthesis of Sulfides from Alkyl Tosylates and Disulfides.*Synthetic Communications* **2004b**, *34(9)*, 1685-1690.

Murray, M. J.; Waters, D. E. Ammonium Chloride-Sodium Sulfide Solutions for OrganicNitro Reductions and for Inorganic Qualitative Analysis.*Journal of AmericanChemical Society* **1938**, *60*, 2818-2819.

Myres, R.H.; Montgomery, D.C. Response Surface Methodology: Process and ProductOptimization Using Designed Experiments, 2nd ed., R.H. Myres, D.C.Montgomery (Eds.), John Wiley and Sons, New York, **2002**.

Naik, S. D.; Doraiswamy, L. K. Mathematical Modeling of Solid-Liquid Phase TransferCatalysis.*Chemical Engineering Science* **1997**, *52(24)*, 4533-4546.

Neumann, R.; Sasson, Y. Mechanism of Base-Catalyzed Reactions in Phase-TransferSystems with Poly (ethy1ene glycols) as Catalysts. The Isomerization ofAllylanisole.*The Journal of Organic Chemistry* **1984**, *49*, 3448-3451.

Niswander, R. H., Edwards, D. J., DuPart, M. S., and Tse, J. P."A More EnergyEfficient Product for Carbon Dioxide Separation," Proceedings of the 42nd Annual Laurance Reid Gas Conditioning Conference, University of Oklahoma,Norman, OK, March 21, **1992.**

Pearce, R. L., and Wolcott, R. A. "Basic Considerations in Acid Gas Removal,"presented at the AIChE Annual Meeting, New Orleans, LA, April 6-10, **1986**.

Plummer, M.A. Process for Recovering Sulfur and Hydrogen from Hydrogen Sulfide.Patent No. WO9412431, **1994**.

Plummer, M.A.; Beazley, P.M. Conversion of Hydrogen Sulfide to Sulfur and Hydrogen.Patent Number US4592905, **1986**.

Plummer, M.A.; Zimmerman, Jr Carle C. Hydrocarbon Desulfurization Process.PatentNumber US4581128, **1986**.

Pradhan, N. C.; Sharma, M. M. Kinetics of Reactions of Benzyl Chloride/p-ChlorobenzylChloride with Sodium Sulfide: Phase-Transfer Catalysis and the Role of theOmega Phase. *Industrial & Engineering Chemistry Research* **1990**, 29, 1103-1108.

Pradhan, N. C.; Sharma, M. M. Solid-Liquid Reactions Catalyzed by Alumina and IonExchange Resin: Reactions of Benzyl Chloride/ p-Chlorobenzyl Chloride withSolid Sodium Sulfide. *Industrial & Engineering Chemistry Research* **1992a**, *31*,1610-1614.

Robin, P. Method for Removing Hydrogen Sulfide From Natural Gas. Patent No.WO9964137, **1999**.

Rumpf, B.; Kamps, Á. P.; Sing, R.; Maurer, G. Simultaneous Solubility of Ammonia andHydrogen Sulfide in Water at Temperatures from 313 K to 393 K. *Fluid PhaseEquilibria***1999**, *158–160*, 923–932.

Satrio, J. A. B.; Doraiswamy, L. K. Phase Transfer Catalysis: A New RigorousMechanistic Model for Liquid-Liquid Systems. *Chemical Engineering Science***2002**, *57*, 1355-

1377.Scott, W. W. Standard Methods of Chemical Analysis, Van Nostrand: New York, 6th ed.,Vol. IIA, p 2181, **1966**.

Sidi-Boumedine, R.; Horstmann, S.; Fischer, K.; Provost, E.; Fürst, W.; Gmehling, J.Experimental determination of hydrogen sulfide solubility data in aqueousalkanolamine solutions.*Fluid Phase Equilibria***2004**, *218*, 149-155.

Starks, C. M. Phase Transfer Catalysis. I. Heterogeneous Reactions Involving AnionTransfer by Quaternary Ammonium and Phosphonium Salts. *Journal of theAmerican Chemical Society* **1971**, *93*, 195-199.

Starks, C. M.; Liotta, C. L. Phase-Transfer Catalysis Principles and Techniques,Academic: New York, **1978**.

Starks, C.M., Liotta, C.L., Halpern, M. Phase Transfer Catalysis. Chapman & Hall, NewYork, USA, **1994**.

Thomas, D.E. Composition and Method for Sweetening Hydrocarbons. Patent No.WO9007467, **1990**.

Thomas, J. C. "Improved Selectivity Achieved with UCARSOL Solvent," Proceedingsof the Laurance Reid Gas Conditioning Conference, University of Oklahoma,Norman, OK, March, **1988**.

Tu, W.; Liu, H.; Tang, Y. The Metal Complex Effect on the Selective Hydrogenation of*m*- and *p*-Chloronitrobenzene Over PVP-Stabilized Platinum Colloidal Catalysts.*Journal of Molecular Catalysis A: Chemical* **2000**, *159*, 115-120.

Vallée, G.; Mougin, P.; Jullian, S.; Fürst, W. Representation of CO_2 and H_2S Absorptionby Aqueous Solutions of Diethanolamine Using an Electrolyte Equation of State.*Industrial & Engineering Chemistry Research* **1999**, *38*, 3473-3480.

Varma, R. S.; Saini, R. K.; Meshram, H. M. Selective Oxidation of Sulfides to SulfoxidesandSulfones by Microwave Thermolysis on Wet Silica-Supported SodiumPeriodate. *Tetrahedron Letters* **1997**, *38 (37)*, 6525-6528.

Volkov, A.G.; Deamer, D. W. Liquid Liquid Interfaces, CRC Press: New York, **1996**.

Volkov, A.G. Interfacial Catalysis, CRC Press: New York, **2002**.

Wang, D. H.; Weng, H. S. Preliminary Study on the Role Played by the Third LiquidPhase in Phase Transfer Catalysis.*Chemical Engineering Science* **1988**, *43*, 2019-2024.

Wang, M.L., Chang, S.W. Model of the kinetics of synthesizing formaldehyde acetals byphase-transfer catalysis. *Industrial & Engineering Chemistry Research* **1994**, *33*,1606–1611.

Wang, M.L; Tseng, Y.H. Phase Transfer Catalytic Reaction of *n*-Bromobutane andSodium Sulfide in a Two-Phase Solution and its Kinetics. *J. Molecular CatalysisA: Chemical* **2003**, *203*, 79–93.

Wang, M.L., Tseng, Y.H. Phase-transfer catalytic reaction of dibromo-o-xylene and 1-butanol in two-phase solution.*Journal of Molecular Catalysis A: Chemical***2002a**, *179*, 17–26.

Wang, M.L., Tseng, Y.H. Kinetic model for synthesizing 4,4-diethanoxy biphenyl byphase transfer catalysis. *Journal of Molecular Catalysis A: Chemical* **2002b**, *188*,51–61.

Wang, M.L., Wu, H.S. Kinetic and mass transfer studies of a sequential reaction by phasetransfer catalysis. *Chemical Engineering Science* **1991**, *46* (2), 509–517.

Wang, M.L., Yang, H.M. Dynamics of phase transfer catalyzed reaction for the allylationof 2,4,6-tribromophenol. *Chemical Engineering Science* **1991a**, *46* (2), 619–627.

Wang, M.L., Yang, H.M. Simplified dynamic model for the allylation of 2,4,6-tribromophenol by phase-transfer catalysis. *Industrial & Engineering ChemistryResearch* **1991b**, *30*, 631–635.

Weber, W. P., Gokel, G. W. Phase Transfer Catalysis in Organic Syntheses.Springer Verlag, NewYork, **1977**.

Weiland, R. H.; Chakravarty, T.; Mather, A. E. Solubility of Carbon Dioxide andHydrogen Sulfide in Aqueous Alkanolamines.*Industrial & EngineeringChemistry Research* **1993**, *32*, 1419-1430.

Wu, H.S., Fang, T.R., Meng, S.S., Hu, K.H. Equilibrium and extraction of quaternary saltin an organic solvent/alkaline solution: effect of NaOH concentration. *Journal ofMolecular Catalysis A: Chemical* **1998**, *136*, 135–146.

Wu, H.S. Phase-plane modeling of a liquid–liquid phase transfer catalyzed reaction.*Industrial & Engineering Chemistry Research* **1993**, *32*, 1323–1327.

Wu, H.S., 1996. Mathematical modeling for liquid–liquid phase-transfer catalysis.Chemical Engineering Science 51 (5), 827–830.

Yadav, G. D.; Lande, S. V. Liquid-liquid-liquid phase transfer catalysis: A novel andgreen concept for selective reduction of substituted nitroaromatics. *AdvancedSynthesis & Catalysis* **2005**, *347*, 1235-1241.

Yadav, G. D.; Lande, S. V. Intensification of Rates and Selectivity Using Tri-liquidversus Bi-liquid Phase Transfer Catalysis: Insight into Reduction of 4-Nitro-oxylenewith Sodium Sulfide. *Industrial & Engineering Chemistry Research* **2007**,*46*, 2951-2961.

Yadav, G. D.; Naik, S. S. Novelties of Liquid-Liquid-Liquid Phase Transfer Catalysis:Alkoxylation of *p*-Chloronitrobenzene. *Catalysis Today* **2001**, *66*, 345-354.

Yadav, G.D., Jadhav, Y.B., 2003a. Kinetics and modeling of liquid–liquid phase transfercatalysed synthesis of p-chlorophenyl acetonitrile: role of co-catalyst inintensification of rates and selectivity. *Journal of Molecular Catalysis A:Chemical* **2003a**, *192*, 41–52.

Yadav, G. D.; Jadhav, Y. B.; Sengupta, S. Novelties of Kinetics and Mechanism ofLiquid–Liquid Phase Transfer Catalyzed Reduction of *p*-Nitroanisole to *p*-Anisidine. *Chemical Engineering Science* **2003b**, *58*, 2681 - 2689.

Yadav, G. D.; Jadhav, Y. B.; Sengupta, S. Selectivity Engineered Phase TransferCatalysis in the Synthesis of Fine Chemicals: Reactions of *p*-Chloronitrobenzenewith Sodium Sulphide. *Journal of Molecular Catalysis A: Chemical* **2003c**, *200*,117-129.

Yadav, G. D.; Reddy, C. A. Kinetics of the n-Butoxilation of *p*-Chloronitrobenzene underLiquid-Liquid-Liquid Phase Transfer Catalysis. *Industrial & EngineeringChemistry Research* **1999**, *38 (6)*, 2245-2253.

Yadav, G. D.; Sharma, M. M. Kinetics of Reactions of Benzyl Chloride with SodiumAcetate/Benzoate: Phase Transfer Catalysis in Solid-Liquid System. *Industrial &Engineering Chemistry Process Design and Development* **1981,** *20*, 385-390.Yang, H.M., Lin, C.L. Phase-transfer catalyzedbenzylation of sodium benzoate usingaliquat 336 as catalyst in liquid–liquid system. *Journal of Molecular Catalysis A:Chemical* **2003**, 206, 67–76.

Yuan, X.; Liu, J.; Zeng, G.; Shi, J.; Huang, G. Optimization of conversion of wasterapeseed oil with high FFA to biodiesel using response surface methodology,*Renew. Energy* **2008**, 33, 1678-1684.